Dear editor and reviewers,

We appreciate all your detail and valuable suggestions on our manuscript (acp-2020-676). We have carefully considered the comments and revised the manuscript accordingly. Please see the point-by-point response below and changes are marked blue in the revised manuscript.

Thanks for your kind help.

Best regards,

Min Hu

Point-by-point response to review comments

Referee #1

This study investigated the emission factors (EFs) and light absorption of carbonaceous components, including water-soluble organic carbon (WSOC), humic-like substances (HULIS), and water-insoluble organic carbon (WISOC), from burning crop residues (wheat and corn). Also, the influences of biofuel moisture and burning conditions on EFs and brown carbon (BrC) absorption were analyzed by using data of modified combustion efficiency (MCE). Although a clear dependence of EFs on MCE values was illustrated, the influence of burning conditions on biomass burning (BB) BrC absorption can hardly be observed or validated. This might be due to the limit in sample number, smoldering combustion conditions (MCE = 0.68 – 0.88), or uncertainties in the calculation of mass absorption efficiency (MAE_λ). Before the acceptance to publication, the following issues should be addressed.

Response: Thanks for your valuable comments on our manuscript and pointing out the deficiency in discussing the influence of burning conditions on biomass burning BrC absorption. We have now carefully revised the manuscript and addressed the following comments.

1. Page 5, line 137. Why total OC was used to represent the concentration of extracted OC?

In Page 127, it was stated that "total OC was analyzed by a thermal/optical carbon analyzer (Subset Laboratory)".

These two "total OC" should be different. The first is used to calculate EFs of OC, while the second is derived for MAE_λ calculation.

Furthermore, the authors can perform better estimation on extracted OC (or WISOC) mass by measuring residue OC on filter samples after solvent extractions. Then the calculation of MAE_λ of WISOC will be less uncertain.

Typically, the residue OC would account for ~10% of the total, and WSOC contributed more than 50% of total OC in this work. Then the inter-sample variability of residue OC will lead to substantial uncertainty on the estimation of WISOC mass and absorption.

Response: Thanks for pointing out the uncertainties in estimating "extracted OC" concentrations. Yes, we used the total OC analyzed by the thermal/optical carbon analyzer to calculate the EFs and also to represent the "total extracted OC" to derive the MAE_λ. We agree with the referee that this may lead to an underestimation of MAE of WISOC, which we mentioned in lines 143-144.

The OC concentration measured by the thermal/optical carbon analyzer has been widely employed to estimate the absorption capability of OC or WISOC extracted by methanol in previous studies (Liu, 2014; Zhu et al., 2018). Chen and Bond (2010) suggested that more than 92% of OC emitted from biomass pyrolysis could be extracted by methanol. Xie et al. (2019) suggested that 93.6%-99.7% of biomass burning-generated OC could be extracted by methanol (added in lines 144-146). Thus, the residue OC was relatively small compared with the methanol-extracted OC, and the difference between the total WISOC (estimated by the difference between thermal/optical carbon analyzer measured OC and WSOC) and methanol-extracted WISOC were relatively small and not taken into consideration in this study.

We agree with the referee that it is very important to estimate the residue OC and make an accurate calculation of WISOC absorption. However, during the extraction procedures in this study, we first cut up the filter samples and then extracted them by water and then methanol. The thermal/optical carbon analyzer quantified OC on certain size filter by converting the carbon species to methane, and measuring by a flame ionization detector. Thus, it's difficult for us to measure the residue OC due to the organic solvent absorbed on the extracted filters and the fragmentized filters after extraction. We will design experiments, such as those conducted in Chen and Bond (2010) and Xie et al. (2019), to estimate the residue OC concentrations and make a more accurate calculation of the MAE of WISOC in our future studies.

Lines 143-146:

"It is noted that the total OC was used to represent the concentration of total extracted OC, which may lead to an underestimation of MAE of WISOC. Previous studies suggested that 92%-99.7% of BBOA could be extracted by methanol (Chen and Bond, 2010; Xie et al., 2019), thus the residue OC un-extracted by methanol was relatively small compared with the extracted fraction."

References:

Chen, Y. and Bond, T. C.: Light absorption by organic carbon from wood combustion, *Atmos. Chem. Phys.*, 10, 1773-1787, 10.5194/acp-10-1773-2010, 2010.

Liu, J., Scheuer, E., Dibb, J., Ziemba, L. D., Thornhill, K. L., Anderson, B. E., Wisthaler, A., Mikoviny, T., Devi, J. J., Bergin, M., and Weber, R. J.: Brown carbon in the continental troposphere, *Geophys. Res. Lett.*, 41, 2191-2195, 10.1002/2013gl058976, 2014.

Xie, M., Chen, X., Hays, M. D., and Holder, A. L.: Composition and light absorption of N-containing aromatic compounds in organic aerosols from laboratory biomass burning, *Atmos Chem Phys*, 19, 2899-2915, 10.5194/acp-19-2899-2019, 2019.

Zhu, C. S., Cao, J. J., Huang, R. J., et al.: Light absorption properties of brown carbon over the southeastern Tibetan Plateau, *Sci. Total Environ.*, 625, 246-251, 10.1016/j.scitotenv.2017.12.183, 2018.

2. The dependence of EFs on burn conditions was well illustrated in Figures 3 and 4. But Figure 7d-f did not show any influence of burn conditions on light absorption. Figure 7a-c and Figure 3b-d tell the same thing——smoldering combustion has higher EFs of carbonaceous aerosols.

Page 11, lines 296-297, "Furthermore, the MAE365 of WSOC and HULIS emitted from straw burning were slightly higher under less efficient burning conditions (Figures 7d, 7e)"

In previous studies, MAE values tend to be greater under more flaming conditions or higher burning temperatures. The observation results reported here seems not reasonable.

Due to the sample number limit and small variability in MAE365 for most observations, the light *absorption of BB BrC did not show any dependence on burn conditions.*

Response: We deleted the statement "*Furthermore, the MAE_{365} of WSOC and HULIS emitted from straw burning were slightly higher under less efficient burning conditions*." in the revised version and revised the sentence as in lines 320-321. We carefully checked the correlation between MAE_{365} and MCE again, and found their correlations were not significant at the 0.01 level (2-tailed) for either WSOC or HULIS. The slight increasing trends of MAE_{365} for WSOC and HULIS as the decreasing of MCE were really due to the two outliers in wheat burning experiments.

We agree with the referee that limited sample number conducted light absorption measurements and small variability in MAE_{365} for most observations may be the reasons for lack of dependence of MAE on burning conditions. We added this reasons in the revised manuscript (lines 310-312). In this study, we intended to simulate the real combustion conditions of agriculture residue burning in the field. Smoldering-dominated conditions, with expected MCE<0.9 or even lower, have been widely observed during the burns of agricultural residues in the agricultural area in China (Figure R1) and India (Figure R2). Thus, the burning conditions were controlled to be dominated by smoldering (as shown in Figure 1, with MCE=0.68-0.88) in our experiments, and the small variation in burning conditions could be the reasons for small variability in MAE_{365} for most observations. More lab-controlled burning experiments, involving larger numbers of experiments and more variable burning conditions, are required in our future studies to address the influence of combustion conditions on the BrC absorption (lines 327-331).

Figure R1 Intense straw burning in agriculture area (Anhui province, China) in China. (Wang, et al., 2017)

Figure R2 Post-harvest crop residue burning in northwest India. (IARI, 2012)

Lines 320-321:

"We did not observe obvious dependence of MAE_{365} on the combustion efficiency for either water-soluble fractions or WISOC (Figure 7d-f)."

Lines 327-331:

"It is noted that limited sample population was selected to conduct the light absorption measurements and smoldering dominated the burning conditions in this study, which could be the reasons that we did not observe an obvious dependence of MAE on combustion conditions. More lab experiments, involving larger numbers of experiments and more variable burning conditions, are required to address the influence of combustion efficiency on light absorption capability of biomass burning-emitted carbonaceous aerosols in future studies."

References:

Crop Residues Management with Conservation Agriculture: Potential, Constraints and Policy Needs, edited by: Institute, I. A. R., India, 2012.

Wang, Y., Hu, M., Lin, P., et al.: Molecular characterization of nitrogen-containing organic compounds in humic-like substances emitted from straw residue burning, *Environ. Sci. Technol.*, 51, 5951-5961, 10.1021/acs.est.7b00248, 2017.

Page 12, lines 339-342, the final conclusion "Our results suggested that the influence of varied combustion efficiency on the emission levels and light absorption of BBOA could surpass the differences between biofuel types. Thus, the burning efficiency or combustion conditions should be taken into consideration when estimate the influence of biomass burning." was not fully supported by the experiments results.

Response: We agree with the referee that the influence of burning conditions on MAE of BBOA was not obvious in this study, as mentioned above. We revised this sentence as follows: "Our results suggested that the influence of varied combustion efficiency on the emission levels of BBOA could surpass the differences between biofuel types. (lines 361-362)". The emission factors of $PM_{2.5}$ or BBOA (OC, WSOC, HULIS) from more smoldering conditions were 2.8-4.3 times of those from more flaming conditions in the present study. While the differences between wheat burning and corn burning under similar combustion conditions (or MCE) were not such obvious, as shown in Figures 3.

Referee #2

The paper by Wang et al. summarizes results on aerosol emission factors and optical properties in burning of agricultural residues (wheat and corn straw) under different burn conditions. They determine the emission factors of $PM_{2.5}$, EC, OC, and different components of OC (water soluble, including HULIS and low-molecular weight oxygenated molecules, and the insoluble fraction) and also determine the wavelength-dependent absorbance, mass absorption efficiency, and Angstrom Exponent of Absorption. They highlight that the EFs of all species except EC was higher at the lower combustion efficiency values (estimated by measurements of CO and CO2) and that the WISOC had the largest contribution to the measured absorbance; however, wavelength dependence of absorption was strongest for the WSOC and HULIS. The results are interesting to the community and the paper fits the scope of ACP. The paper is overall well written although some parts benefit from some editing (I suggest below). I'd like the authors to clarify the points I highlight below before the paper is accepted for publication:

Response: Thanks for your valuable comments on our manuscript. We have now carefully revised the manuscript and addressed the following points.

Technical points:

L76-77: I think this statement underestimates all the studies that have been carried out in the Fire lab in Missoula, that characterize influence of combustion efficiency on aerosol optical properties. I can imagine that for agricultural residue burning, the studies are limited, so a more accurate statement should be included here.

Response: Thanks for the kind reminding. We added the related studies from the Fire lab in Missoula in lines 59-60, and revised this statement to be more accurate (lines 77-79).

Lines 59-60:

"The light absorption of biomass burning aerosols are also largely dependent on the combustion conditions (Cheng et al., 2016a; Liu et al., 2014; Pokhrel et al., 2016; Saleh et al., 2014)."

Lines 77-79:

"However, few studies have been conducted to gain a comprehensive understanding on the influence of combustion conditions on the chemical composition and light absorption of different BBOA fractions from agricultural residue burning."

L110-111: Do authors mean that fuels were weighed before and after drying? If so please add this detail.

Response: Yes, the fuels were weighed before and after drying. We have added this detail and revised this sentence as follows: "The moisture content was measured by weighing the fuels before and after drying the biofuels in the oven at 105℃ for 24 h." (lines 112-113)

Table S1: There doesn't seem to be a consistent picture between MCE and the moisture content. For example, MCE ~0.77 was observed at all different moisture content values of the wheat. Please explain the reason for this variability. Because of this lack of obvious trend, I would not mention this in the conclusions either (L318-319)

Response: We plotted the variations of MCE as a function of moisture contents (added in Figure S2 in the supporting information) and checked their correlation. The MCE generally decreased as moisture contents increased (Pearson correlation=0.73 at the 0.01 significance level). Burning conditions are not only influenced by biofuel moisture contents, but also biofuel structures (e.g., biomass sizes), combustion temperatures and ambient conditions, etc. (Chen and Bond, 2010; Lu et al., 2009; Sanchis et al., 2014) The variations in other factors could be the reasons for observing similar MCE values under different moisture contents. To exclude the influence of other factors, we thus conducted three parallel experiments under each condition (the same type of straw with the same level of moisture content, as listed in Table S1).

We added the explanation in lines 178-183, and revised the related sentence in the conclusion section (Line 330).

Lines 178-183:

"Similar MCE was also observed among wheat burning experiments with different levels of moisture contents (Table S1). This was because that MCE is not only influenced by biofuel moisture contents but also the variations of biofuel structures (e.g. size), burning temperatures or ambient conditions (Chen and Bond, 2010; Lu et al., 2009; Sanchis et al., 2014). We cannot completely exclude the differences of other factors between each parallel experiment, which was the reason for repeating each condition for three times in our experiment (Table S1)."

Line 342:

"The emission levels, compositions and light absorption of BBOA were influenced by the burning conditions."

Newly added Figure S2 in the supporting information:

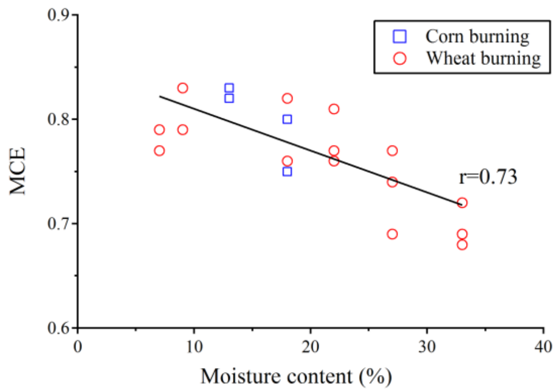

Figure S2 Variations of MCE as a function of moisture contents. The Pearson correlation=0.73 at the 0.01 significance level.

References:

Chen, Y. and Bond, T. C.: Light absorption by organic carbon from wood combustion, *Atmos. Chem. Phys.*, 10, 1773-1787, 10.5194/acp-10-1773-2010, 2010.

Lu, H., Zhu, L., and Zhu, N.: Polycyclic aromatic hydrocarbon emission from straw burning and the influence of combustion parameters, *Atmos. Environ.*, 43, 978-983, 10.1016/j.atmosenv.2008.10.022, 2009.

Sanchis, E., Ferrer, M., Calvet, S., et al.: Gaseous and particulate emission profiles during controlled rice straw burning, *Atmos. Environ.*, 98, 25-31, 10.1016/j.atmosenv.2014.07.062, 2014.

Eqn of Abs(l): why is absorbance at 700 nm subtracted from the absorbance at the wavelength of interest? Why should this be a relative absorbance? Shouldn't the absorbance at a specific wavelength be corrected for the background absorbance at the same wavelength while sampling only pure water?

Response: Yes, the spectrum and absorption at a specific wavelength were determined and corrected relative to a reference cuvette which contained the same extraction solvent (water or methonal) during the measurement. Abs_{700} (no absorption for BrC extracts) is subtracted from Abs_{λ} to correct the systematic baseline drift of the of the instrument (Xie et al., 2017; Xie et al., 2019; Zhang et al., 2013; Zhu et al., 2018) (added in lines 139-140).

Lines 139-140:

"A_{λ} is referenced to the A_{700} to account for systematic baseline drift (Xie et al., 2019; Zhang et al., 2013)."

References:

Xie, M., Hays, M. D., and Holder, A. L.: Light-absorbing organic carbon from prescribed and laboratory biomass burning and gasoline vehicle emissions, *Scientific Reports*, 7, 7318, 10.1038/s41598-017-06981-8, 2017.

Xie, M., Chen, X., Hays, M. D., and Holder, A. L.: Composition and light absorption of N-containing aromatic compounds in organic aerosols from laboratory biomass burning, *Atmos Chem Phys*, 19, 2899-2915, 10.5194/acp-19-2899-2019, 2019.

Zhu, C. S., Cao, J. J., Huang, R. J., et al: Light absorption properties of brown carbon over the southeastern Tibetan Plateau, *Sci. Total Environ.*, 625, 246-251, 10.1016/j.scitotenv.2017.12.183, 2018.

L178-180: The average EFs of corn are higher, but still considering the variabilities that were observed for both fuels, the difference isn't significant and beyond the observed variabilities.

Response: Thanks for the reminding. We have removed this statement in the revised version.

Fig. 3g: why not showing all the fits as in the other panels? Also, are the fits a double-sided regression line, considering the uncertainties in the x and y values?

Response: We have revised Figure 3g to show all the fits as in the other panels. Yes, all the fits are Pearson correlations considering the uncertainties in the x and y values. We have added the significant levels (2-tailed) in the revised figure.

Revised Figure 3:

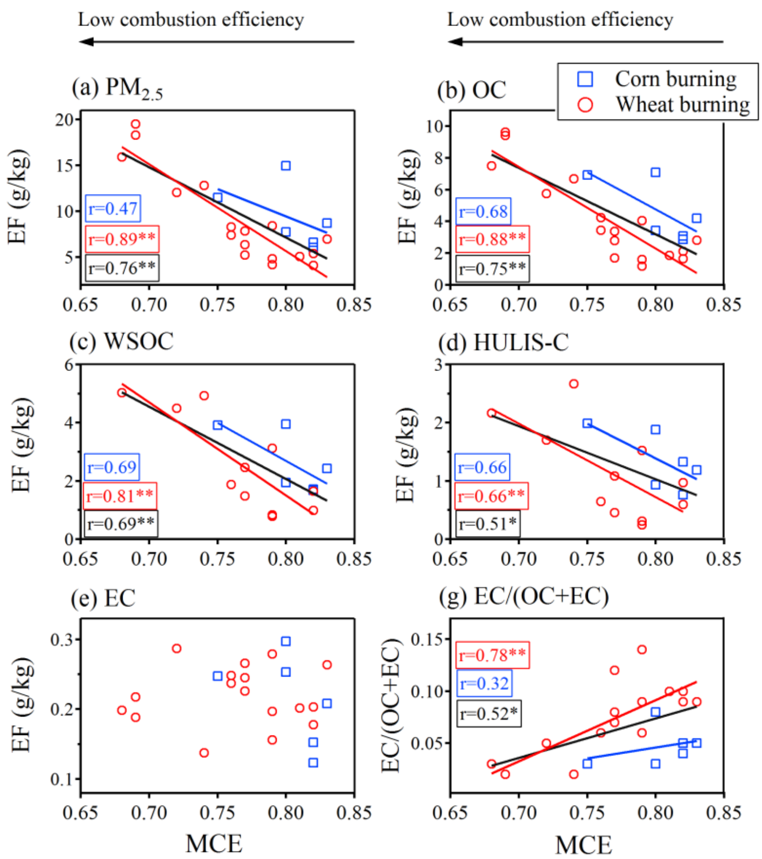

Figure 3 Emission factors of $PM_{2.5}$, carbonaceous aerosols (OC, WSOC, $HULIS_C$ and EC) and EC/(OC+EC) ratios as a function of modified combustion efficiency (MCE). Corn and wheat burning emissions are denoted by red and blue colors, respectively. The r values in each panel are the Pearson correlations between emission factors and MCE for corn (blue), wheat (red) and the overall (black) burning experiments. The ** or * following the r value indicates the correlation is significant at the 0.01 level or 0.05 level (2-tailed).

L233: what precluded the possibility of having burns with MCE>0.9 that's more representative of flaming conditions? I think some discussion should be provided.
Also it would be valuable to mention what the expected MCE in real world burns of agricultural residues are so readers get an idea of how applicable the results are and what values are most meaningful to be used in models.

Response: We are afraid that the reviewer may misread our writing: "As the conducted experiments were mostly dominated by smoldering combustions (MCE=0.68-0.88) in this study, we CANNOT EXCLUDE the possibility that the EC emissions may be higher under flaming-dominated combustions (e.g. MCE>0.9)." (lines 252-253) Though we observed flaming-dominated conditions during the initial period of low-moisture biomass burning experiment (as shown in Figure 1a), the whole combustion period was generally dominated by smoldering conditions based on the averaged MCE of 0.68-0.88 in this study.

Smoldering-dominated conditions, with expected MCE<0.9 or even lower, have been widely observed during the real world burns of agricultural residues in the agricultural area in China (Figure R1) and India (Figure R2). Thus, we believe our results, obtained under smoldering-dominated conditions (MCE=0.68-0.88), are applicable to the field or related model studies. Referring the observed or expected MCE or EC/OC ratios in specific study would help to select more suitable values in models. We have added the description in lines 170-172.

Figure R1 Intense straw burning in agriculture area (Anhui province, China) in China. (Wang, et al., 2017)

Figure R2 Post-harvest crop residue burning in northwest India. (IARI, 2012)

Lines 170-172:

"Smoldering-dominated conditions, with expected MCE<0.9 or even lower, have been widely observed during the combustion of agricultural residues in the field (IARI, 2012; Wang et al., 2017), thus the results in this study are applicable to the field or related model studies."

References:

Crop Residues Management with Conservation Agriculture: Potential, Constraints and Policy Needs, edited by: Institute, I. A. R., India, 2012.

Wang, Y., Hu, M., Lin, P., et al: Molecular characterization of nitrogen-containing organic compounds in humic-like substances emitted from straw residue burning, *Environ. Sci. Technol.*, 51, 5951-5961, 10.1021/acs.est.7b00248, 2017.

Figure 4. There are some wheat burns for which the K+/OC and Cl-/OC ratios are highly variable; are all the burns from the same batch of fuel? Could this variability be explained by variable K and Cl content of the fuel itself?

Response: Yes, all the wheat burns are from the same batch of biofuels. Thus, the differences in the K and Cl contents of biofuels among different experiments may be small.

Previous studies suggested that the contents of K and Cl released into smokes are related to elevated combustion temperatures during the biomass burning. The K and Cl begin to be released into the smokes when fire temperatures are higher than certain values (e.g. Temp.>600-700℃ for K, and Temp.> 200℃ for Cl), and the released proportion increase as the combustion temperatures further increased (Jensen et al., 2000; Knudsen et al., 2004). We checked the burning conditions of the two experiments with high K^+/OC and Cl^-/OC ratios. The moisture contents were 7% (the lowest moisture level in our experiments) and MCE of the two experiments were 0.77 and 0.79. Though the average MCE is not the highest, high fire temperatures were observed during the initial flaming combustion periods of the two low-moisture biomass burning experiments (added in Figure S4). The temperatures during these periods were much higher than the smoldering periods. We think that the higher ratios of released K and Cl were related to the elevated combustion temperatures during the initial flaming periods. We measured the fire temperatures using a sensor above the fires (as shown in Figure S1), the real combustion temperatures could be higher than the measured ones (e.g. higher than 600-700℃, which were suggested to be the K released temperatures during biomass burning). We have added the explanation in lines 266-268 and Figure S4.

Lines 273-275:

"The two wheat burning experiments (moisture content=7%) with higher K^+/OC and Cl^-/OC ratios (>0.5) than others were related to the higher combustion temperatures during the initial flaming periods of the burning experiments (Figure S4)."

Newly added Figure S4 in the supporting information:

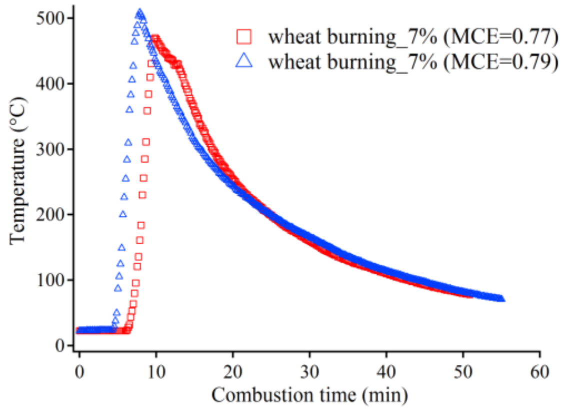

Figure S4 Variations of measured fire temperatures during two wheat straw (moisture content=7%) burning experiments with MCE=0.77 and 0.79.

L290-291: Since this paper has reported on MAE as well as EF of the different components of OC, it will be very valuable to combine the two results and present the EF of absorption to be able to more directly compare radiative impacts of WISOC, WSOC, and HULIS.

Response: We estimated the radiation effects of WISOC, WSOC and HULIS relative to elemental carbon using a simplified model in the revised manuscript. Related descriptions have been added in section 2.3 (lines 149-155) and lines 313-314.

Lines 149-155 in section 2.3:

"The radiation effects of different BrC fractions (WSOC, HULIS and WISOC) relative to elemental carbon (EC, f) were estimated using a simplified model (Kirillova et al., 2014; Wu et al., 2020):

$$f = \frac{\int I_0(\lambda)\left\{1-e^{-\left(MAE_{BrC,365}\left(\frac{365}{\lambda}\right)^{AAE}\cdot C_{BrC}\cdot h_{ABL}\right)}\right\}d\lambda}{\int I_0(\lambda)\left\{1-e^{-\left(MAE_{EC,870}\left(\frac{870}{\lambda}\right)\cdot C_{EC}\cdot h_{ABL}\right)}\right\}d\lambda} \qquad (3)$$

where $MAE_{BrC,365}$ and $MAE_{EC,870}$ represent the MAE of different BrC fractions at 365 nm and MAE of EC at 870 nm. AAE is the AAE values of different BrC fractions obtained in this study, and the AAE of EC is set to 1. C_{BrC} and C_{EC} are the concentrations of BrC and EC, and h_{ABL} is the height of atmospheric boundary layer (1000 m). $I_0(\lambda)$ represents the clear sky Air Mass 1 Global Horizontal solar irradiance (Levinson et al., 2010)."

Lines 313-314:

"The solar energy absorbed by biomass burning-emitted WISOC relative to EC (25%) among the wavelength range of 300-700 nm was higher than those of WSOC (10%) or HULIS (4%)."

L297-298, 338-339: I disagree; there are really two points that might be considered as outliers and without those, the MAE(365) vs MCE looks pretty flat. I suggest removing this statement.

Response: Thanks for the reminding. We carefully checked the correlations between MAE_{365} and MCE again, and found their correlations were not significant at the 0.01 level (2-tailed) for either WSOC or HULIS. As suggested, we have removed this statement in the revised version.

Suggested Edits:

L 33: remove observed in "..were also observed higher under. . ."

Response: Revised accordingly.

L39 and 334: remove if in "if without considering the burning conditions. . ."

Response: Removed accordingly.

L 61: Add ". . .was reported to be higher for more . . ."

Response: Added accordingly.

L112: consider changing "weighted" to "weighed"

Response: Changed accordingly.

L118: include the volumetric unit for both 10 and 5 units of water and methanol, respectively.

Response: Revised accordingly.

L121: why did you use a smaller size filter for the WISOC fraction?

Response: We used a smaller size filter to extract the WISOC fraction for further analysis using HPLC-MS. It's just a test experiment this time due to the limited samples, and we plan to characterize the molecular compositions of water-insoluble BrC in our future studies.

L129-L130: consider changing "minus. . ." to "difference between total OC and WSOC."

Response: Changed accordingly.

Eqns. Consider adding equation numbers

Response: We have added the equation numbers in the revised manuscript.

L174-175: I think I know what the authors try to say (in higher moisture fuel burns, some energy is first used to dry up the fuel and so the temperature is lower); however, as written the sentence is confusing. Consider rephrasing it.

Response: The sentence is now revised as: "In higher-moisture fuel burns, some energy released from the combustion is first used to dry up the higher moistures of the biofuels, thus the fire temperatures and burning efficiency were lower than those of the low-moisture biomass burning." (lines 195-197)

L186 and 191: change negligible to "neglected"

Response: Revised accordingly.

L200, 315: change "dominated" to "dominant"

Response: Changed accordingly. I think you may mean changing "negligible" to "neglected" in line 315 (line 339 in the revised version).

L234-235: rephrase the beginning of the sentence; the structure is not correct

Response: The sentence is now revised as: "Though the EC emission factors did not show obvious variation trends as a function of MCE, a positive correlation between EC/(OC+EC) ratios and combustion efficiency was observed (Figure 3g)." (lines 254-255)

L237: data "are"...

Response: Revised accordingly.

L247: remove "that"

Response: Removed as suggested.

L272: consider changing "occupy" to "contribute to"

Response: Changed accordingly.

L271-273: the % contributions are for 300 nm and 400 nm, respectively? It's unclear when a range of 300-400nm is mentioned. Please clarify.

Response: Thanks for pointing out the unclear statement. The % contributions here are for the $HULIS_C$ and high-polarity WSOC fractions, respectively. To be clear, the sentence is now revised as: "In the wavelength range of 300-400 nm, $HULIS_C$ and other high-polarity WSOC (WSOC-h=WSOC-$HULIS_C$) respectively contribute to 16%-28% and 1%-10% of the total BBOA absorption for corn burning, and 17%-29% and 12%-15% for wheat burning." (lines 294-296)

L296, 338: change "as the decreasing of MCE" to "... as MCE decreases..."

Response: Revised accordingly.

Chemical composition and light absorption of carbonaceous aerosols emitted from crop residue burning: Influence of combustion efficiency

Yujue Wang,[1] Min Hu,[*,1,2,4] Nan Xu,[1] Yanhong Qin,[1] Zhijun Wu,[1,2] Liwu Zeng,[3] Xiaofeng Huang,[3] Lingyan He [3]

[1]State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China

[2]Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Nanjing University of Information Science & Technology, Nanjing, China

[3]Key Laboratory for Urban Habitat Environmental Science and Technology, School of Environment and Energy, Peking University Shenzhen Graduate School, Shenzhen, China

[4]Beijing Innovation Center for Engineering Sciences and Advanced Technology, Peking University, Beijing 100871, China

Correspondence to: Min Hu (minhu@pku.edu.cn)

Abstract. Biomass burning is one of the major sources of carbonaceous aerosols, which affects air quality, radiation budget and human health. Field straw residue burning is a widespread type of biomass burning in Asia, while its emissions are poorly understood compared with the wood burning emissions. In this study, lab-controlled straw (wheat and corn) burning experiments were designed to investigate the emission factors and light absorption properties of different biomass burning organic aerosol (BBOA) fractions, including water soluble organic carbon (WSOC), humic-like substances (HULIS) and water insoluble organic carbon (WISOC). The influences of biofuel moisture content and combustion efficiency on emissions are comprehensively discussed. The emission factors of $PM_{2.5}$, OC and EC were 9.3±3.4, 4.6±1.9 and 0.21±0.07 g/kg for corn burning and 8.7±5.0, 3.9±2.8 and 0.22±0.05 g/kg for wheat burning, generally lower than wood or forest burning emissions. Though the mass contribution of WISOC among OC (32%-43%) was lower than WSOC, the light absorption contribution of WISOC (57%–84% @300-400 nm) surpassed WSOC due to the higher mass absorption efficiency (MAE) of WISOC. The results suggested that BBOA light absorption would be largely underestimated if only considering the water soluble fractions. However, the light absorption of WSOC among near-UV ranges, occupying 39%-43% of the total extracted OC absorption at 300 nm, cannot be negligible due to the sharper increase of absorption towards shorter wavelength compared with WISOC. HULIS were the major light absorption contributors among WSOC, due to the higher MAE of HULIS than other high-polarity WSOC components. The emission levels and light absorption of BBOA were largely influenced by the burning conditions, indicated by modified combustion efficiency (MCE) calculated by measured CO and CO_2 in this study. The emission factors of $PM_{2.5}$, OC, WSOC, HULIS and organic acids were enhanced under lower-MCE conditions or during higher-moisture straw burning experiments. Light absorption coefficients of BBOA at 365

nm were also higher under lower-MCE conditions, which was mainly due to the elevated mass emission factors. Our results suggested that the influence of varied combustion efficiency on particle emissions could surpass the differences caused by different types of biofuels. Thus, the burning efficiency or conditions should be taken into consideration when estimating the influence of biomass burning. In addition, we observed that the ratios of K^+/OC and Cl^-/OC increased under higher-MCE conditions due to the enhancement of released potassium and chlorine under higher fire temperatures during flaming combustion. This indicates that potassium ion, as a commonly used biomass burning tracer, may lead to estimation uncertainty without considering the burning conditions.

1 Introduction

Biomass burning emissions, as a major primary source of carbonaceous aerosols, have significant effects on the air quality, human health as well as regional or global radiation budget (Bond, 2004; Chen et al., 2017a; Reid et al., 2005; Saleh et al., 2015). Biomass burning could contribute one-third of the black carbon (BC) budget and two-thirds of the primary organic aerosol budget on the global scale (Bond, 2004; Bond et al., 2013). In recent years, biomass burning organic aerosols (BBOA) also attracted much attention due to their substantial contribution to light-absorbing organic aerosols, known as brown carbon (BrC) (Andreae and Gelencsér, 2006; Laskin et al., 2015; Lin et al., 2016; Saleh et al., 2014; Washenfelder et al., 2015; Yan et al., 2018). Emission factors (EF) of BrC ranged from 1.0 to 1.4 g/kg biomass, comparable to those of BC (Aurell and Gullett, 2013). Majority of BrC aerosol mass was associated with biomass burning emissions in rural southeast US (Washenfelder et al., 2015). Regional radiative forcing effects of BrC could be comparable to those of BC over major areas dominated by biomass burning and biofuel combustion, such as South and East Asia (Feng et al., 2013).

Emission factors, chemical compositions and light absorption properties of biomass burning aerosols could be obviously influenced by different types of biomass, biofuel structures, moisture contents, and especially varied burning conditions (Chen and Bond, 2010; Holder et al., 2016; Reisen et al., 2018). The emissions of particulate organics could span several orders of magnitude depending on different burning conditions (Chen et al., 2017a; Jen et al., 2019). In general, higher levels of particulate matters (PM) and organic aerosols were emitted during less efficient biomass burning, due to prolonged incomplete or smoldering combustion (Holder et al., 2016; Jen et al., 2019; Reisen et al., 2018). Open biomass burning, especially smoldering combustion, dominates the organic carbon (OC) emissions in many regions of the world on an annual-average basis (Bond, 2004). The light absorption of biomass burning aerosols are also largely dependent on the combustion conditions (Cheng et al., 2016a; Liu et al., 2014; Pokhrel et al., 2016; Saleh et al., 2014). The contribution of BrC to aerosol light absorption at near-UV wavelength was reported to be higher for more smoldering combustion compared with more flaming combustion (Holder et al., 2016). The reported variation trends of BBOA absorption properties as a function of combustion conditions, however, are not consistent from different studies. High variability in reported emission factors and optical properties of BBOA from different burning conditions complicates their treatment in climate models (Liu et al., 2014; Saleh et al., 2014), and indicates the importance of further investigations on biomass burning emissions, especially the influence of burning conditions.

Unlike the well-understood BC, the light-absorbing OC or BrC comprise a wide range of poorly characterized organic compounds, which exhibit highly variable chemical and light absorption properties (Andreae and Gelencsér, 2006; Laskin et al., 2015; Lin et al., 2016; Saleh et al., 2014; Washenfelder et al., 2015; Yan et al., 2018). Previous studies have suggested that methanol extracted BrC were usually more light-absorbing than water extracts for BBOA or ambient aerosols (Chen and Bond, 2010; Liu et al., 2013). More than 92% of the light absorbing OC emitted from solid fuel pyrolysis could be extracted by methanol, compared with 73% for water-extracted compounds (Chen and Bond, 2010). Alkaline or methanol extracted OC fractions were also observed with higher mass absorption efficiency (MAE) at 365 nm than water soluble organic carbon (WSOC) for residential coal combustion (Li et al., 2018). Only considering the water soluble BrC would result in underestimation of BrC absorption and radiative forcing (Cheng et al., 2016b; Cheng et al., 2017). Different light absorption properties of organic fractions could be attributed to the varied chemical compositions and structures (Chen et al., 2016a; Chen et al., 2016b; Chen et al., 2017b). However, few studies have been conducted to gain a comprehensive understanding on the influence of combustion conditions on the chemical composition and light absorption of different BBOA fractions from agricultural residue burning.

Field open burning of agriculture wastes or crop residues is a widespread type of biomass burning in Asia (IARI, 2012; Bond, 2004; Streets et al., 2003a). Open crop residue burning during harvest season would result in severely adverse impacts on regional air quality and human health (Chen et al., 2017a; Li et al., 2014; Lin and Yu, 2011; Streets et al., 2003b; Zhang et al., 2010). The PM emission factors from agricultural waste burning range from 1.7 to 17.8 g/kg (Bond, 2004). Source apportionment results showed that ~50% of carbonaceous aerosols in Beijing were associated with biomass burning, with crop residue combustion as a major source (Cheng et al., 2013). Straw residue burning could contribute as high as 51% of PM and 76% of OC during harvest seasons in the agriculture regions in China (Li et al., 2014). Considering the large contribution of straw residue burning, the chemical compositions and light absorption properties of BBOA in Asia may differ from other regions with wood burning as the major type of biomass burning. However, the understanding on field straw residue burning emissions is still limited. A better characterization of the emission levels and optical properties of straw burning aerosols is required to quantify their effects on air quality and regional radiation forcing in agriculture areas (Hungershoefer et al., 2008). Laboratory simulation experiment has been suggested as a good way to study biomass burning emissions due to its advantage in quantifying emission factors and controlling combustion conditions within well-defined limits. In this study, a series of lab burning experiments were designed to systematically investigate the emission factors, chemical compositions and light absorption properties of both water-soluble and water-insoluble carbonaceous aerosols emitted from straw residue burning. The influence of biofuel moisture contents, burning conditions and combustion efficiency on the BBOA emission levels and light absorption properties are comprehensively discussed.

2 Methods

2.1 Simulation and sampling of biomass burning aerosols

Lab-controlled burning experiments were conducted in the Laboratory of Biomass Burning Simulation at Peking University Shenzhen Graduate School. The simulation system was designed and optimized on the basis of the one used in He et al. (2010) (He et al., 2010), which included combustion system, dilution system, sampling system and data acquisition system (Figure S1). During each experiment, about 1-2 kg biomass fuels were ignited on the combustion pan. The emitted smoke was collected by the hood above the fire, and diluted by zero air (21 mol% O_2 and 79 mol % N_2) before collected on filters or monitored by online instruments. Smoke aerosols were collected on both Teflon (Whatman Inc.) and quartz fiber (Whatman Inc.) filters, using a $PM_{2.5}$ cutoff with a sampling flow rate of 16.7 L/min. During each burning experiment, CO and CO_2 were measured continuously by CO and CO_2 analyzers (Thermo Scientific Inc., Bremen, Germany). The burning efficiency, calculated based on the online CO and CO_2 data, were monitored continuously during each experiment (Table S1). The variation of fire temperatures during each experiment was also measured by a sensor above the fire (Figure S1).

In this study, corn and wheat, two kinds of primary grain crops in China, burning was simulated to represent the straw residue burning in China. To investigate the influence of biofuel moisture contents on burning emissions, straws with different levels of moisture contents were burned, including low (13%) and high (18%) levels for corn burning experiments, low (7%-9%), medium (18%-22%), and high (27%-33%) levels for wheat burning experiments (Table S1). The moisture content was measured by weighing the fuels before and after drying the biofuels in the oven at 105℃ for 24 h. Straw residues with different moisture contents were prepared by mixing weighed biofuels with weighed pure water in a plastic box, and shaking until the water was absorbed. Each experiment condition was repeated three times. All the conducted experiment conditions as well as burning conditions are summarized in Table S1.

2.2 Isolation of carbonaceous aerosols

The quartz fiber filters were used to extract different carbonaceous aerosol fractions, including water-insoluble organic carbon (WISOC), WSOC, and carbon component of HUmic-Like Substances ($HULIS_C$). The filter samples were firstly extracted in an ultrasonic bath twice using 10 mL, and 10 mL ultrapure water, each time for 30 min. The extracts were then combined and filtered with a 0.45 μm pore size syringe filter (Gelman Sciences) to obtain the WSOC solutions. After removing the WSOC fraction on filters, the WISOC fractions were then extracted in an ultrasonic bath twice using 5 mL, and 5 mL methanol, each time for 30 min. The extracts then were combined and filtered using a 0.25 μm syringe filter. The HULIS fraction was isolated from the WSOC solutions via solid phase extraction (SPE), with majority of low molecular weight organic acids (with relatively higher polarities) and sugars removed from the water solutions. Details about the HULIS extraction procedures were described in our previous paper (Wang et al., 2017). The WSOC fraction excluded HULIS was named as high-polarity WSOC (WSOC-h) in this study.

2.3 Quantification and light absorption measurements of carbonaceous aerosols

The total OC abundance was analyzed by a thermal/optical carbon analyzer (Sunset Laboratory). The concentrations of water soluble carbonaceous aerosol fractions, including WSOC and $HULIS_C$, were measured using a total organic carbon (TOC) analyzer (AnalytikJena multi N/C 3100). The WISOC concentrations were obtained by the difference between total OC and WSOC. Light absorption of the extracted solutions (WSOC, $HULIS_C$ and WISOC) were measured by a UV-vis spectrometer (UV-1780, Shimadzu) over the wavelength range of 300-700 nm. The absorptions of WSOC and WISOC were added up to represent the absorption of the total extracted OC. The absorption coefficients (Abs_λ, Mm^{-1}) and mass absorption efficiency (MAE_λ) of isolated solutions at a wavelength λ were calculated as follow (Cheng et al., 2011; Cheng et al., 2016b):

$$Abs_\lambda = (A_\lambda - A_{700})\frac{V_{\mathrm{sol}}}{V_{air}\times \mathrm{L}} \times \ln(10) \quad (1)$$

$$MAE_\lambda = \frac{Abs_\lambda}{C} \quad (2)$$

where A_λ and A_{700} represent the measured absorbance at wavelength λ and 700 nm. A_λ is referenced to the A_{700} to account for systematic baseline drift (Xie et al., 2019; Zhang et al., 2013). V_{sol} is the volume of extracted solutions and V_{air} is the volume of air sampled through the filter punch. The optical path length (L) is 1 cm in the present experiments. Ln (10) is used to convert from common logarithm to natural logarithm. C corresponds to the concentrations of OC, WISOC, WSOC or $HULIS_C$ fractions. It is noted that the total OC was used to represent the concentration of total extracted OC, which may lead to an underestimation of MAE of WISOC. Previous studies suggested that 92%-99.7% of BBOA could be extracted by methanol (Chen and Bond, 2010; Xie et al., 2019), thus the residue OC un-extracted by methanol was relatively small compared with the extracted fraction. The wavelength dependence of light absorption is described using the Absorption Angstrom Exponent (AAE), which is calculated by a linear regression fit of $\log(Abs_\lambda)$ versus $\log(\lambda)$ in the wavelength range of 300-450 nm.

The radiation effects of different BrC fractions (WSOC, HULIS and WISOC) relative to elemental carbon (EC, f) were estimated using a simplified model (Kirillova et al., 2014; Wu et al., 2020):

$$f = \frac{\int I_0(\lambda)\left\{1-e^{-\left(MAE_{BrC,365}\left(\frac{365}{\lambda}\right)^{AAE}\cdot C_{BrC}\cdot h_{ABL}\right)}\right\}d\lambda}{\int I_0(\lambda)\left\{1-e^{-\left(MAE_{EC,870}\left(\frac{870}{\lambda}\right)\cdot C_{EC}\cdot h_{ABL}\right)}\right\}d\lambda} \quad (3)$$

where $MAE_{BrC,365}$ and $MAE_{EC,870}$ represent the MAE of different BrC fractions at 365 nm and MAE of EC at 870 nm. AAE is the AAE values of different BrC fractions obtained in this study, and the AAE of EC is set to 1. C_{BrC} and C_{EC} are the concentrations of BrC and EC, and h_{ABL} is the height of atmospheric boundary layer (1000 m). $I_0(\lambda)$ represents the clear sky Air Mass 1 Global Horizontal solar irradiance (Levinson et al., 2010).

Water-soluble K^+, Cl^- and low molecular weight organic acids (acetic acid, formic acid, succinic acid, oxalic acid, propionic acid and methanesulfonic acid) were analyzed by ion chromatograph (DIONEX, ICS2500/ICS2000), following the procedures described in Guo et al. (2010) (Guo et al., 2010).

3 Results and discussion

3.1 Burning conditions and combustion efficiency

The burning conditions and combustion efficiency, calculated by measured CO and CO_2 concentrations, of the simulation experiments are shown in Figure 1 and Table S1. Modified combustion efficiency (MCE), defined as $\Delta CO_2/(\Delta CO_2+\Delta CO)$, is used to indicate the burning conditions during a fire (Akagi et al., 2011; Andreae and Merlet, 2001). The burning conditions in this study varied from different fires, with the MCE ranging from 0.68 to 0.88 and an average value of 0.77. The amount and compositions of substances emitted from a given fire are determined to a large extent by the burning conditions or the ratio of flaming to smoldering combustion, which is often expressed as "combustion efficiency". Higher MCE (>0.9) indicates more flaming combustions, and lower MCE indicates more smoldering conditions. A previous study suggested that pure flaming has an MCE near 0.99, and the MCE of most smoldering combustion is around or lower than 0.8 (Akagi et al., 2011). The burning experiments were generally dominated by smoldering combustions in the present study. Smoldering-dominated conditions, with expected MCE<0.9 or even lower, have been widely observed during the combustion of agricultural residues in the field (IARI, 2012; Wang et al., 2017), thus the results in this study are applicable to the field or related model studies.

The biomass fuels with lower moisture contents are generally burned more efficiently, with relatively higher MCE values (Table S1, Figure S2), which suggested higher proportion of flaming combustion during the fire. The MCE of higher-moisture biomass burning was generally lower, and prolonged smoldering combustion was observed (Figures 1, S2).

Previous lab-controlled burning experiments also reported similar phenomenon that higher fuel moistures would lower the combustion efficiency, shorten flaming phase and introduce prolonged smoldering combustion (Chen et al., 2010). The relative proportion of flaming versus smoldering phases can vary considerably as a function of fuel moistures. Similar MCE was also observed among wheat burning experiments with different levels of moisture contents (Table S1). This was because that MCE is not only influenced by biofuel moisture contents but also the variations of biofuel structures (e.g. size), burning temperatures or ambient conditions (Chen and Bond, 2010; Lu et al., 2009; Sanchis et al., 2014). We cannot completely exclude the differences of other factors between each parallel experiment, which was the reason for repeating each condition for three times in our experiment (Table S1).

Figure 1 displays variations of the monitored parameters (CO, CO_2, $\Delta CO/\Delta CO_2$ and fire temperature) during two selected burning experiments (low-moisture biomass burning with MCE=0.83, and high-moisture biomass burning with MCE=0.68). Different burning conditions dominate at different periods of a fire and the length of each period varied by experiments (Figure 1). Actually, flaming and smoldering phases occur simultaneously during a fire and the proportions of different combustion types vary over time (Akagi et al., 2011; Andreae and Merlet, 2001). For example, the initial period of low-moisture biomass burning experiment (Figure 1a) is dominated by flaming, wherein CO_2 increased rapidly to the highest level and $\Delta CO/\Delta CO_2$ ratios were lower (MCE was higher) compared with the smoldering-dominated period. The fire temperatures were very high during this initially high-efficiency burning period. During the later period, smoldering dominated the burning conditions. The burning efficiency and fire temperatures decreased during this period, and $\Delta CO/\Delta CO_2$ ratios were higher than the first period. Previous ground-based and aircraft measurements of wildfire emissions also observed gradually decreased combustion efficiency of a fire over time (Collier et al., 2016). For the high-moisture biomass burning, smoldering combustion dominated the fire types during the whole period (Figure 1b). In higher-moisture fuel burns, some energy released from the combustion is first used to dry up the higher moistures of the biofuels, thus the fire temperatures and burning efficiency were lower than those of the low-moisture biomass burning.

3.2 Emission factors of carbonaceous aerosols

The average emission factors of $PM_{2.5}$, OC and EC were 9.3±3.4, 4.6±1.9 and 0.21±0.07 g/kg for corn burning and 8.7±5.0, 3.9±2.8 and 0.22±0.05 g/kg for wheat burning (Figure 2). The measured emission factors in this study fall within the range of previous straw burning experiments (4.7-12.9, 1.2-8.9, 0.17-1.2 g/kg for $PM_{2.5}$, OC and EC, respectively)(Akagi et al., 2011; Hays et al., 2005; Li et al., 2007). The estimated EFs from crop residue burning were generally lower than wood or forest burning emissions (Akagi et al., 2011; Aurell and Gullett, 2013; Jen et al., 2019). However, open crop residue burning in the field could result in severe air pollution during harvest season, especially in agriculture areas in China and South Asia (IARI, 2012; Li et al., 2014; Streets et al., 2003a; Venkataraman et al., 2006). This type of biomass burning cannot be neglected in these regions.

Organic matter (OM), calculated by multiplying OC by 1.3 (Li et al., 2007), was the dominant component of straw burning aerosols, which accounted for ~64% and ~55% of the $PM_{2.5}$ emitted from corn and wheat burning (Figure 2). Around 57% and 68% of the OC from corn and wheat burning are water soluble, and $HULIS_C$ represent 53% and 46% of the WSOC. Though the mass contributions of WISOC were lower than WSOC in straw burning aerosols (Figure 2), the WISOC fractions cannot be neglected, especially for considering the light absorption properties of BBOA (see section 3.4). Previous studies also suggested a large portion of WISOC in ambient aerosols, which are important contributor of light-absorbing BrC (Cheng et al., 2016b; Cheng et al., 2017).

The average EFs of water-soluble acetic acid, formic acid, succinic acid and oxalic acid were respectively 13.3±13.9, 4.1±3.3, 8.8±10.6, 2.2±1.1 mg/kg for corn burning and 13.0±14.5, 4.7±5.3, 9.9±13.5, 3.1±1.9 mg/kg for wheat burning (Figure 2). Propionic acid and methanesulfonic acid in most samples were below the instrument detection limits in this study, and their emissions were not taken into consideration in the following discussion. The quantified water-soluble low-molecular-weight acids averagely accounted for 0.84% (0.16%-1.6%) and 0.88% (0.24%-1.8%) of the water-soluble OM (WSOM) emitted from corn and wheat burning. Previous study has suggested that low molecular weight organic acids represented an important fraction of WSOC in BBOA, and oxalic acid was a dominant short dicarboxylic (C2-C6) acids (Falkovich et al., 2005). The estimated emission factors of acetic acid and formic acid in this work were lower than those emitted from eucalypt forest fires, which were reported 17 and 26 mg/kg for flaming combustion, and 104 and 94 mg/kg for smoldering combustion based on ground-based field measurements (Reisen et al., 2018). The difference could be attributed to different biofuels, burning conditions as well as conducted experimental methods.

Figure 2 compares the emission factors of $PM_{2.5}$, carbonaceous aerosols and low molecular weight organic acids from straw residue burning under different levels of moisture contents. The EFs of fine particles and organic carbonaceous aerosols from high-moisture biomass burning were obviously higher than those from low-moisture biomass burning. Substantial particulate carbonaceous aerosols could be generated from burning of higher-moisture biofuels, which is mainly associated with the prolonged smoldering phases and less efficient combustions (Figure 1, Table S1). Similar variation trends were also reported in previous biomass burning studies (Chen et al., 2010; Sanchis et al., 2014). Different levels of biofuel moisture contents will actually influence the burning conditions, and thus impact the emission levels and compositions of particulate matters.

3.3 Influence of combustion efficiency on emission factors

As shown in Figure 3, the emission factors of $PM_{2.5}$ and organic carbonaceous components increased with decreasing MCE. Particle emissions were obviously enhanced under less efficient burning conditions. The emission factors of $PM_{2.5}$, OC, WSOC and $HULIS_C$ from the most smoldering combustion experiment were about 3.4, 4.3, 3.8 and 2.8 times of those from the most flaming combustion condition, regardless of the biomass types. The emissions of low molecular weight organic acids also follow the similar variation trends with combustion efficiency as those of OC or WSOC emission factors (Figure S3). These trends are generally in agreement with previous studies (Dhammapala et al., 2006; Holder et al., 2016; Jen et al., 2019; Reisen et al., 2018; Wang et al., 2013). Under the same burning conditions, the emission factors of particles or organic aerosols from corn burning were slightly higher than those from wheat burning (Figure 3). This was mainly due to the different pyrolysis temperatures and combustion efficiency of different biofuels, which would influence the burning processes (Khan et al., 2009; Zanatta et al., 2016). Our results suggested that the influence of varied burning conditions or combustion efficiency on particle emissions could surpass the differences between the two types of straw residue burning measured in this study (Figure 3). Thus, the burning efficiency or conditions should be taken into consideration when simulate or estimate the influence of biomass burning emissions in future models.

Different from organic compounds, the emission factors of EC under different combustion efficiency remain relatively consistent (Figure 3e). Holder et al. (2016) summarized the results from lab and field studies, and also found that the black carbon emission factors from different studies are relatively constant, despite the differences in plume dilution or measurement methods (Holder et al., 2016). Some studies, however, reported an increasing trend in EC or BC emission levels with the increasing of combustion efficiency in wildfires or forest burns in U.S. (Aurell and Gullett, 2013; Jen et al., 2019). As the conducted experiments were mostly dominated by smoldering combustions (MCE=0.68-0.88) in this study, we cannot exclude the possibility that the EC emissions may be higher under flaming-dominated combustions (e.g. MCE>0.9). Though the EC emission factors did not show obvious variation trends as a function of MCE, a positive correlation between EC/(OC+EC) ratios and combustion efficiency was observed (Figure 3g). Due to the obvious dependence of EC/OC or EC/(OC+EC) ratios on burning efficiency, these ratios could be employed to indicate different burning conditions when the emitted CO and CO_2 data are not available, which have been used in previous studies (Xie et al., 2018; Xie et al., 2019).

To further investigate the influence of burning conditions on the chemical compositions of biomass burning aerosols, mass ratios of WSOC/OC, $HULIS_C$/OC, K^+/OC and Cl^-/OC as a function of burning efficiency are plotted in Figure 4. The WSOC/OC and $HULIS_C$/OC mass ratios ranged from 0.52-0.78 and 0.16-0.54 among different burning experiments. The $HULIS_C$/OC ratios were comparable to those (0.26-0.44, with an average of 0.34) reported in field or controlled chamber combustion experiments (Lin et al., 2010). We did not observe obvious variation trends of WSOC/OC or $HULIS_C$/OC ratios with MCE (Figure 4), which indicated relative constant BBOA chemical compositions under different combustion conditions. However, the K^+/OC and Cl^-/OC ratios showed consistent variation trends under different MCE conditions, which increased from <0.1 under the more smoldering condition to >0.5 under the more flaming condition for K^+/OC, and from 0.05 to >0.5 for Cl^-/OC (Figure 4). The highest K^+/OC (0.64) and Cl^-/OC (0.61) ratios were observed in a low-moisture wheat burning experiment with a MCE of 0.79. This is because the K and Cl emissions from combustion are highly affected by fire temperatures and burning conditions. Lab-controlled experiments suggested that the proportions of released potassium and chlorine from the biomass fuels increase with the applied combustion temperatures (Jensen et al., 2000; Knudsen et al., 2004). The flaming combustion (with higher MCE) was observed much higher fire temperatures than the smoldering combustion (with lower MCE) (Figure 1). Though the emission levels of particles or organic aerosols decreased during higher efficiency burning (Figure 3), elevated proportions of potassium and chlorine were released into smokes during the flaming combustion phase under this condition (Figure 4b). The two wheat burning experiments (moisture content=7%) with higher K^+/OC and Cl^-/OC ratios (>0.5) than others were related to the higher combustion temperatures during the initial flaming periods of the burning experiments (Figure S4). Potassium ion is a commonly used tracer to indicate the biomass burning emissions. However, our results revealed that K^+ cannot correctly indicate the emission levels of biomass burning aerosols under obviously different burning conditions, which may lead to large uncertainty in estimating burning emissions if without considering the combustion conditions.

3.4 Light absorption of BBOA

The light absorption of straw burning organic aerosols decreased sharply from near-UV to visible wavelengths (Figure 5), indicating their properties as biomass burning-generated BrC. The absorption of WISOC, WSOC and $HULIS_C$ at 300 nm was as high as 4.5, 15.2 and 11.2 times of those at 400 nm for corn burning emissions, and 4.8, 9.2 and 10.6 times for wheat burning emissions. The wavelength dependence property of BBOA light absorption was described by AAE derived from the absorption in the range of 300-450 nm. The AAE of WISOC, WSOC and $HULIS_C$ were respectively 5.8-5.9, 8.6-11.3, 8.9-10.2 for corn burning aerosols and 5.7-6.0, 8.1-9.0, 9.0-10.5 for wheat burning aerosols, and the averaged values were also shown in Figure 5. The water-soluble BBOA fractions (WSOC and HULIS) showed stronger wavelength dependence than the water insoluble fractions. The estimated AAE values of straw burning organic aerosols in this study are comparable to those of BBOA (5.3-8.1) and biomass burning-influenced atmospheric aerosols (5.2-9.4) reported in previous studies (Hecobian et al., 2010; Hoffer et al., 2006; Wu et al., 2018; Wu et al., 2019; Xie et al., 2017; Xie et al., 2019; Zhu et al., 2018). The strong light absorption of biomass burning-generated BrC in near-UV range would lead to an increase in aerosol light absorption and radiative forcing efficiency (Chakrabarty et al., 2010).

The WISOC was the most important light-absorption fraction among straw burning organic aerosols, which contributed 61%–84% and 57%–72% of the light absorption (@300-400 nm) by extracted BrC emitted from corn and wheat burning (Figure 5). In the wavelength range of 300-400 nm, $HULIS_C$ and other high-polarity WSOC (WSOC-h=WSOC-$HULIS_C$) respectively contribute to 16%-28% and 1%-10% of the total BBOA absorption for corn burning, and 17%-29% and 12%-15% for wheat burning. Though the mass contribution of WISOC was lower than WSOC (Figure 2), the light absorption of

WISOC surpassed WSOC due to the higher light absorption capability of water-insoluble BBOA, indicated by the higher MAE of WISOC (Figure 6). Meanwhile, the light absorption of water-soluble BBOA among near-UV ranges cannot be neglected due to their sharper increase of absorption towards shorter wavelength compared with WISOC (Figure 5). The light absorption contribution of WSOC to extracted BrC increased substantially from 16%-28% at 400 nm to 39%-43% at 300 nm. Among the water-soluble BBOA, HULIS were the major contributors of light absorption, which occupied 74% and 68% of the WSOC absorption at 300 nm for corn and wheat burning emissions, respectively. This was due to the higher light absorption capability of HULIS than other high-polarity WSOC fractions (Figure 6), though their mass contributions were comparable in straw burning aerosols (Figure 2).

The light absorption capabilities of different BBOA fractions are compared in Figure 6. The estimated MAE_{365} values of straw burning-generated BrC in this study are comparable to those reported in previous studies (Fan et al., 2018; Xie et al., 2017). The MAE of WISOC are higher than water-soluble BBOA (WSOC and HULIS) among the measured wavelength ranges for both corn and wheat burning aerosols. The MAE_{300} of WISOC was 1.6 and 1.7 times of WSOC emitted from corn and wheat burning, and comparable to those of HULIS (Figure 6). Due to the slower decrease of WISOC absorption towards visible wavelengths than the water-soluble fractions (Figure 5), the MAE_{365} of WISOC was as high as 2.5 and 2.2 times of WSOC from corn and wheat burning emissions, and 1.7 and 1.6 times of HULIS. Though the mass contribution of WISOC among BBOA could be smaller than WSOC, their contribution to light absorption cannot be neglected due to the higher MAE of water insoluble BBOA. The solar energy absorbed by biomass burning-emitted WISOC relative to EC (25%) among the wavelength range of 300-700 nm was higher than those of WSOC (10%) or HULIS (4%). The light absorption of BBOA would be largely underestimated if only considering the water soluble fractions. Previous studies also reported a large proportion of WISOC absorption in BBOA and ambient aerosols (Cheng et al., 2016b; Cheng et al., 2017; Park et al., 2018; Sengupta et al., 2018).

Figure 7 clearly shows the dependence of BBOA absorption coefficient (Abs_{365}) on burning conditions. Higher Abs_{365} of biomass burning-generated BrC were observed under less efficient burning conditions for both corn and wheat burning experiments. This is mainly due to the elevated BBOA emission factors as MCE decreases (Figure 3). We did not observe obvious dependence of MAE_{365} on the combustion efficiency for either water-soluble fractions or WISOC (Figure 7d-f). Previous lab and field studies suggested that the optical properties of biomass burning aerosols are more dependent on burning conditions other than fuel types (Liu et al., 2014; Xie et al., 2017). The MAE_{365} of BBOA emitted from flaming combustion were reported higher than those from smoldering combustion based on lab-controlled burning experiments (Xie et al., 2019). Another lab experiment also suggested the dependence of MAE_{365} of methanol-extracted BBOA on burning conditions, while the variation trends are different regarding different fuel types or sampling methods among different experiments (Xie et al., 2017). It is noted that limited sample population was selected to conduct the light absorption measurements and smoldering dominated the burning conditions in this study, which could be the reasons that we did not observe an obvious dependence of MAE on combustion conditions. More lab experiments, involving larger numbers of experiments and more variable burning conditions, are required to address the influence of combustion efficiency on light absorption capability of biomass burning-emitted carbonaceous aerosols in future studies.

4 Conclusions

The emission factors of $PM_{2.5}$, OC and EC were 9.3, 4.6 and 0.21 g/kg for corn burning and 8.7, 3.9 and 0.22 g/kg for wheat burning, generally lower than wood or forest burning emissions. Around 57% and 68% of the OC emitted from corn and wheat burning are WSOC, among which $HULIS_C$ represent 53% and 46% of the WSOC mass concentrations. Though the mass contribution of WISOC was lower than WSOC, the light absorption contribution of WISOC (57%–84% @300-400 nm) surpassed WSOC due to the higher MAE of WISOC. The BBOA light absorption would be largely underestimated if only considering the water soluble fractions. Meanwhile, the light absorption of WSOC among near-UV ranges, occupying 39%-43% of extracted OC absorption at 300 nm, cannot be neglected due to their sharper increase of absorption towards shorter wavelength compared with WISOC. HULIS were the major light absorption contributors among WSOC, and their light absorption capability was higher than other high-polarity WSOC components.

The emission levels, compositions and light absorption of BBOA were influenced by the burning conditions. The combustion conditions varied from different burning experiments, with the MCE ranging from 0.68 to 0.88. The emission factors of $PM_{2.5}$ and organic carbonaceous aerosols were obviously enhanced under less efficient burning conditions (lower MCE). The emission factors of $PM_{2.5}$, OC, WSOC and $HULIS_C$ from the most smoldering combustion experiment were about 3.4, 4.3, 3.8 and 2.8 times of those from the most flaming combustion condition, regardless of the biofuel types employed in this study. The emission factors of $PM_{2.5}$ and carbonaceous aerosols from high-moisture straw burning were obviously elevated compared with those from low-moisture straw burning experiments. This is mainly due to the prolonged smoldering and incomplete combustion period during high-moisture biomass burning.

The EC/(EC+OC) ratios showed a positive correlation with MCE, though EC emission factors remain relative constant under different combustion conditions. Thus, it is reasonable to employ EC/OC or EC/(EC+OC) ratios as an indicator of biomass burning conditions. The mass ratios of WSOC/OC or $HULIS_C$/OC did not display obvious variation trends under different combustion efficiency. However, the K^+/OC and Cl^-/OC ratios showed continuous increasing trends during higher efficiency burning, from <0.1 under the more smoldering condition to >0.5 under the more flaming condition for K^+/OC, and from 0.05 to >0.5 for Cl^-/OC ratios. This is mainly attributed to the elevated proportions of released potassium and chlorine from biofuels under the higher fire temperatures during flaming combustions. Our results indicate that potassium ion, as a commonly used biomass burning tracer, may lead to large uncertainty in estimating biomass burning emission levels without considering the combustion conditions.

Higher absorption coefficient (Abs_{365}) of straw burning-generated BrC, including WSOC, HULIS and WISOC, were observed under less efficient burning conditions for both corn and wheat burning. This is mainly attributed to the higher BBOA emission factors as MCE decreases. Our results suggested that the influence of varied combustion efficiency on the emission levels of BBOA could surpass the differences between biofuel types. Thus, the burning efficiency or combustion conditions should be taken into consideration when estimate the influence of biomass burning.

Data availability. The data presented in this article are available from the authors upon request (minhu@pku.edu.cn).

The Supplement related to this article is available online

Author contributions. MH, ZW, XH, and LH organized the project. YW conducted the simulation experiments. YW, NX and YQ analyzed the samples. YW wrote the manuscript with input from all co-authors. All authors contributed to discussing the results and commenting on the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgements. This study was supported by National Natural Science Foundation of China (91844301, 91544214), and the project funded by China Postdoctoral Science Foundation (2019M650354). We also thank Dr. Song Guo for his helpful suggestions on this study.

References:

Crop Residues Management with Conservation Agriculture: Potential, Constraints and Policy Needs, edited by: Institute, I. A. R., India, 2012.

Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J. D., and Wennberg, P. O.: Emission factors for open and domestic biomass burning for use in atmospheric models, Atmos. Chem. Phys., 11, 4039-4072, 10.5194/acp-11-4039-2011, 2011.

Andreae, M. O. and Merlet, P.: Emission of trace gases and aerosols from biomass burning, Global Biogeochem. Cy., 15, 955-966, Doi 10.1029/2000gb001382, 2001.

Andreae, M. O. and Gelencsér, A.: Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols, Atmos. Chem. Phys., 6, 3131-3148, 10.5194/acp-6-3131-2006, 2006.

Aurell, J. and Gullett, B. K.: Emission factors from aerial and ground measurements of field and laboratory forest burns in the southeastern US: $PM_{2.5}$, black and brown carbon, VOC, and PCDD/PCDF, Environ. Sci. Technol., 47, 8443-8452, 10.1021/es402101k, 2013.

Bond, T. C.: A technology-based global inventory of black and organic carbon emissions from combustion, J. Geophys. Res., 109, 10.1029/2003jd003697, 2004.

Bond, T. C., Doherty, S. J., Fahey, D. W., Forster, P. M., Berntsen, T., DeAngelo, B. J., Flanner, M. G., Ghan, S., Kärcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P. K., Sarofim, M. C., Schultz, M. G., Schulz, M., Venkataraman, C., Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S. K., Hopke, P. K., Jacobson, M. Z., Kaiser, J. W., Klimont, Z., Lohmann, U., Schwarz, J. P., Shindell, D., Storelvmo, T., Warren, S. G., and Zender, C. S.: Bounding the role of black carbon in the climate system: A scientific assessment, J. Geophys. Res., [Atmos.], 118, 5380-5552, 10.1002/jgrd.50171, 2013.

Chakrabarty, R. K., Moosmüller, H., Chen, L. W. A., Lewis, K., Arnott, W. P., Mazzoleni, C., Dubey, M. K., Wold, C. E., Hao, W. M., and Kreidenweis, S. M.: Brown carbon in tar balls from smoldering biomass combustion, Atmos. Chem. Phys., 10, 6363-6370, 10.5194/acp-10-6363-2010, 2010.

Chen, J., Li, C., Ristovski, Z., Milic, A., Gu, Y., Islam, M. S., Wang, S., Hao, J., Zhang, H., He, C., Guo, H., Fu, H., Miljevic, B., Morawska, L., Thai, P., Lam, Y. F., Pereira, G., Ding, A., Huang, X., and Dumka, U. C.: A review of biomass burning: Emissions and impacts on air quality, health and climate in China, Sci. Total Environ., 579, 1000-1034, 10.1016/j.scitotenv.2016.11.025, 2017a.

Chen, L. W. A., Verburg, P., Shackelford, A., Zhu, D., Susfalk, R., Chow, J. C., and Watson, J. G.: Moisture effects on carbon and nitrogen emission from burning of wildland biomass, Atmos. Chem. Phys., 10, 6617-6625, 10.5194/acp-10-6617-2010, 2010.

Chen, Q., Ikemori, F., Higo, H., Asakawa, D., and Mochida, M.: Chemical Structural Characteristics of HULIS and Other Fractionated Organic Matter in Urban Aerosols: Results from Mass Spectral and FT-IR Analysis, Environ. Sci. Technol., 50, 1721-1730, 10.1021/acs.est.5b05277, 2016a.

Chen, Q., Ikemori, F., and Mochida, M.: Light Absorption and Excitation-Emission Fluorescence of Urban Organic Aerosol Components and Their Relationship to Chemical Structure, Environ. Sci. Technol., 50, 10859-10868, 10.1021/acs.est.6b02541, 2016b.

Chen, Q., Ikemori, F., Nakamura, Y., Vodicka, P., Kawamura, K., and Mochida, M.: Structural and Light-Absorption Characteristics of Complex Water-Insoluble Organic Mixtures in Urban Submicrometer Aerosols, Environ. Sci. Technol., 51, 8293-8303, 10.1021/acs.est.7b01630, 2017b.

Chen, Y. and Bond, T. C.: Light absorption by organic carbon from wood combustion, Atmos. Chem. Phys., 10, 1773-1787, 10.5194/acp-10-1773-2010, 2010.

Cheng, Y., He, K. B., Zheng, M., Duan, F. K., Du, Z. Y., Ma, Y. L., Tan, J. H., Yang, F. M., Liu, J. M., Zhang, X. L., Weber, R. J., Bergin, M. H., and Russell, A. G.: Mass absorption efficiency of elemental carbon and water-soluble organic carbon in Beijing, China, Atmos. Chem. Phys., 11, 11497-11510, 10.5194/acp-11-11497-2011, 2011.

Cheng, Y., Engling, G., He, K. B., Duan, F. K., Ma, Y. L., Du, Z. Y., Liu, J. M., Zheng, M., and Weber, R. J.: Biomass burning contribution to Beijing aerosol, Atmos. Chem. Phys., 13, 7765-7781, 10.5194/acp-13-7765-2013, 2013.

Cheng, Y., Engling, G., Moosmüller, H., Arnott, W. P., Chen, L. W. A., Wold, C. E., Hao, W. M., and He, K.-b.: Light absorption by biomass burning source emissions, Atmos. Environ., 127, 347-354, 10.1016/j.atmosenv.2015.12.045, 2016a.

Cheng, Y., He, K.-b., Du, Z.-y., Engling, G., Liu, J.-m., Ma, Y.-l., Zheng, M., and Weber, R. J.: The characteristics of brown carbon aerosol during winter in Beijing, Atmos. Environ., 127, 355-364, 10.1016/j.atmosenv.2015.12.035, 2016b.

Cheng, Y., He, K. B., Engling, G., Weber, R., Liu, J. M., Du, Z. Y., and Dong, S. P.: Brown and black carbon in Beijing aerosol: Implications for the effects of brown coating on light absorption by black carbon, Sci. Total Environ., 599-600, 1047-1055, 10.1016/j.scitotenv.2017.05.061, 2017.

Collier, S., Zhou, S., Onasch, T. B., Jaffe, D. A., Kleinman, L., Sedlacek, A. J., 3rd, Briggs, N. L., Hee, J., Fortner, E., Shilling, J. E., Worsnop, D., Yokelson, R. J., Parworth, C., Ge, X., Xu, J., Butterfield, Z., Chand, D., Dubey, M. K., Pekour, M. S., Springston, S., and Zhang, Q.: Regional Influence of Aerosol Emissions from Wildfires Driven by Combustion Efficiency: Insights from the BBOP Campaign, Environ. Sci. Technol., 50, 8613-8622, 10.1021/acs.est.6b01617, 2016.

Dhammapala, R., Claiborn, C., Corkill, J., and Gullett, B.: Particulate emissions from wheat and Kentucky bluegrass stubble burning in eastern Washington and northern Idaho, Atmos. Environ., 40, 1007-1015, 10.1016/j.atmosenv.2005.11.018, 2006.

Falkovich, A. H., Graber, E. R., Schkolnik, G., Rudich, Y., Maenhaut, W., and Artaxo, P.: Low molecular weight organic acids in aerosol particles from Rondônia, Brazil, during the biomass-burning, transition and wet periods, Atmos. Chem. Phys., 5, 781-797, 10.5194/acp-5-781-2005, 2005.

Fan, X., Li, M., Cao, T., Cheng, C., Li, F., Xie, Y., Wei, S., Song, J., and Peng, P. a.: Optical properties and oxidative potential of water- and alkaline-soluble brown carbon in smoke particles emitted from laboratory simulated biomass burning, Atmos. Environ., 194, 48-57, 10.1016/j.atmosenv.2018.09.025, 2018.

Feng, Y., Ramanathan, V., and Kotamarthi, V. R.: Brown carbon: a significant atmospheric absorber of solar radiation?, Atmos. Chem. Phys., 13, 8607-8621, 10.5194/acp-13-8607-2013, 2013.

Guo, S., Hu, M., Wang, Z. B., Slanina, J., and Zhao, Y. L.: Size-resolved aerosol water-soluble ionic compositions in the summer of Beijing: implication of regional secondary formation, Atmos. Chem. Phys., 10, 947-959, 10.5194/acp-10-947-2010, 2010.

Hays, M. D., Fine, P. M., Geron, C. D., Kleeman, M. J., and Gullett, B. K.: Open burning of agricultural biomass: Physical and chemical properties of particle-phase emissions, Atmos. Environ., 39, 6747-6764, 10.1016/j.atmosenv.2005.07.072, 2005.

He, L. Y., Lin, Y., Huang, X. F., Guo, S., Xue, L., Su, Q., Hu, M., Luan, S. J., and Zhang, Y. H.: Characterization of high-resolution aerosol mass spectra of primary organic aerosol emissions from Chinese cooking and biomass burning, Atmos. Chem. Phys., 10, 11535-11543, 10.5194/acp-10-11535-2010, 2010.

Hecobian, A., Zhang, X., Zheng, M., Frank, N., Edgerton, E. S., and Weber, R. J.: Water-Soluble Organic Aerosol material and the light-absorption characteristics of aqueous extracts measured over the Southeastern United States, Atmos. Chem. Phys., 10, 5965-5977, 10.5194/acp-10-5965-2010, 2010.

Hoffer, A., Gelencsér, A., Guyon, P., Kiss, G., Schmid, O., Frank, G. P., Artaxo, P., and Andreae, M. O.: Optical properties of humic-like substances (HULIS) in biomass-burning aerosols, Atmos. Chem. Phys., 6, 3563-3570, 10.5194/acp-6-3563-2006, 2006.

Holder, A. L., Hagler, G. S. W., Aurell, J., Hays, M. D., and Gullett, B. K.: Particulate matter and black carbon optical properties and emission factors from prescribed fires in the southeastern United States, J. Geophys. Res., [Atmos.], 121, 3465-3483, 10.1002/2015jd024321, 2016.

Hungershoefer, K., Zeromskiene, K., Iinuma, Y., Helas, G., Trentmann, J., Trautmann, T., Parmar, R. S., Wiedensohler, A., Andreae, M. O., and Schmid, O.: Modelling the optical properties of fresh biomass burning aerosol produced in a smoke chamber: results from the EFEU campaign, Atmos. Chem. Phys., 8, 3427-3439, 10.5194/acp-8-3427-2008, 2008.

Jen, C. N., Hatch, L. E., Selimovic, V., Yokelson, R. J., Weber, R., Fernandez, A. E., Kreisberg, N. M., Barsanti, K. C., and Goldstein, A. H.: Speciated and total emission factors of particulate organics from burning western US wildland fuels and their dependence on combustion efficiency, Atmos. Chem. Phys., 19, 1013-1026, 10.5194/acp-19-1013-2019, 2019.

Jensen, P. A., Frandsen, F. J., Dam-Johansen, K., and Sander, B.: Experimental Investigation of the Transformation and Release to Gas Phase of Potassium and Chlorine during Straw Pyrolysis, Energ Fuel, 14, 1280-1285, 10.1021/ef000104v, 2000.

Khan, A. A., de Jong, W., Jansens, P. J., and Spliethoff, H.: Biomass combustion in fluidized bed boilers: Potential problems and remedies, Fuel Processing Technology, 90, 21-50, 10.1016/j.fuproc.2008.07.012, 2009.

Kirillova, E. N., Andersson, A., Tiwari, S., Srivastava, A. K., Bisht, D. S., and Gustafsson, Ö.: Water-soluble organic carbon aerosols during a full New Delhi winter: Isotope-based source apportionment and optical properties, J. Geophys. Res., [Atmos.], 119, 3476-3485, 10.1002/2013jd020041, 2014.

Knudsen, J. N., Jensen, P. A., and Dam-Johansen, K.: Transformation and release to the gas phase of Cl, K, and S during combustion of annual biomass, Energ Fuel, 18, 1385-1399, 10.1021/ef049944q, 2004.

Laskin, A., Laskin, J., and Nizkorodov, S. A.: Chemistry of atmospheric brown carbon, Chem. Rev., 115, 4335-4382, 10.1021/cr5006167, 2015.

Levinson, R., Akbari, H., and Berdahl, P.: Measuring solar reflectance—Part I: Defining a metric that accurately predicts solar heat gain, Solar Energy, 84, 1717-1744, 10.1016/j.solener.2010.04.018, 2010.

Li, J. F., Song, Y., Mao, Y., Mao, Z. C., Wu, Y. S., Li, M. M., Huang, X., He, Q. C., and Hu, M.: Chemical characteristics and source apportionment of $PM_{2.5}$ during the harvest season in eastern China's agricultural regions, Atmos. Environ., 92, 442-448, 10.1016/j.atmosenv.2014.04.058, 2014.

Li, M., Fan, X., Zhu, M., Zou, C., Song, J., Wei, S., Jia, W., and Peng, P.: Abundances and light absorption properties of brown carbon emitted from residential coal combustion in China, Environ. Sci. Technol., 53, 595-603, 10.1021/acs.est.8b05630, 2018.

Li, X., Wang, S., Duan, L., Hao, J., Li, C., Chen, Y., and Yang, L.: Particulate and trace gas emissions from open burning of wheat straw and corn stover in China, Environ. Sci. Technol., 41, 6052-6058, 10.1021/es0705137, 2007.

Lin, P., Engling, G., and Yu, J. Z.: Humic-like substances in fresh emissions of rice straw burning and in ambient aerosols in the Pearl River Delta Region, China, Atmos. Chem. Phys., 10, 6487-6500, 10.5194/acp-10-6487-2010, 2010.

Lin, P. and Yu, J. Z.: Generation of reactive oxygen species mediated by humic-like substances in atmospheric aerosols, Environ. Sci. Technol., 45, 10362-10368, 10.1021/es2028229, 2011.

Lin, P., Aiona, P. K., Li, Y., Shiraiwa, M., Laskin, J., Nizkorodov, S. A., and Laskin, A.: Molecular characterization of brown carbon in biomass burning aerosol particles, Environ. Sci. Technol., 50, 11815-11824, 10.1021/acs.est.6b03024, 2016.

Liu, J., Bergin, M., Guo, H., King, L., Kotra, N., Edgerton, E., and Weber, R. J.: Size-resolved measurements of brown carbon in water and methanol extracts and estimates of their contribution to ambient fine-particle light absorption, Atmos. Chem. Phys., 13, 12389-12404, 10.5194/acp-13-12389-2013, 2013.

Liu, S., Aiken, A. C., Arata, C., Dubey, M. K., Stockwell, C. E., Yokelson, R. J., Stone, E. A., Jayarathne, T., Robinson, A. L., DeMott, P. J., and Kreidenweis, S. M.: Aerosol single scattering albedo dependence on biomass combustion efficiency: Laboratory and field studies, Geophys. Res. Lett., 41, 742-748, 10.1002/2013gl058392, 2014.

Lu, H., Zhu, L., and Zhu, N.: Polycyclic aromatic hydrocarbon emission from straw burning and the influence of combustion parameters, Atmos. Environ., 43, 978-983, 10.1016/j.atmosenv.2008.10.022, 2009.

Park, S., Yu, G.-H., and Lee, S.: Optical absorption characteristics of brown carbon aerosols during the KORUS-AQ campaign at an urban site, Atmos. Res., 203, 16-27, 10.1016/j.atmosres.2017.12.002, 2018.

Pokhrel, R. P., Wagner, N. L., Langridge, J. M., Lack, D. A., Jayarathne, T., Stone, E. A., Stockwell, C. E., Yokelson, R. J., and Murphy, S. M.: Parameterization of single-scattering albedo (SSA) and absorption Ångström exponent (AAE) with EC / OC for aerosol emissions from biomass burning, Atmos. Chem. Phys., 16, 9549-9561, 10.5194/acp-16-9549-2016, 2016.

Reid, J. S., Eck, T. F., Christopher, S. A., Koppmann, R., Dubovik, O., Eleuterio, D. P., Holben, B. N., Reid, E. A., and Zhang, J.: A review of biomass burning emissions part III: intensive optical properties of biomass burning particles, Atmos. Chem. Phys., 5, 827-849, 10.5194/acp-5-827-2005, 2005.

Reisen, F., Meyer, C. P., Weston, C. J., and Volkova, L.: Ground-Based Field Measurements of $PM_{2.5}$ Emission Factors From Flaming and Smoldering Combustion in Eucalypt Forests, J. Geophys. Res., [Atmos.], 10.1029/2018jd028488, 2018.

Saleh, R., Robinson, E. S., Tkacik, D. S., Ahern, A. T., Liu, S., Aiken, A. C., Sullivan, R. C., Presto, A. A., Dubey, M. K., Yokelson, R. J., Donahue, N. M., and Robinson, A. L.: Brownness of organics in aerosols from biomass burning linked to their black carbon content, Nature Geosci., 7, 647-650, 10.1038/ngeo2220, 2014.

Saleh, R., Marks, M., Heo, J., Adams, P. J., Donahue, N. M., and Robinson, A. L.: Contribution of brown carbon and lensing to the direct radiative effect of carbonaceous aerosols from biomass and biofuel burning emissions, J. Geophys. Res., [Atmos.], 120, 10.1002/2015jd023697, 2015.

Sanchis, E., Ferrer, M., Calvet, S., Coscollà, C., Yusà, V., and Cambra-López, M.: Gaseous and particulate emission profiles during controlled rice straw burning, Atmos. Environ., 98, 25-31, 10.1016/j.atmosenv.2014.07.062, 2014.

Sengupta, D., Samburova, V., Bhattarai, C., Kirillova, E., Mazzoleni, L., Iaukea-Lum, M., Watts, A., Moosmüller, H., and Khlystov, A.: Light absorption by polar and non-polar aerosol compounds from laboratory biomass combustion, Atmos. Chem. Phys., 18, 10849-10867, 10.5194/acp-18-10849-2018, 2018.

Streets, D. G., Yarber, K. F., Woo, J. H., and Carmichael, G. R.: Biomass burning in Asia: Annual and seasonal estimates and atmospheric emissions, Global Biogeochem. Cy., 17, Artn 1099 10.1029/2003gb002040, 2003a.

Streets, D. G., Yarber, K. F., Woo, J. H., and Carmichael, G. R.: Biomass burning in Asia: Annual and seasonal estimates and atmospheric emissions, Global Biogeochem. Cy., 17, n/a-n/a, 10.1029/2003gb002040, 2003b.

Venkataraman, C., Habib, G., Kadamba, D., Shrivastava, M., Leon, J. F., Crouzille, B., Boucher, O., and Streets, D. G.: Emissions from open biomass burning in India: Integrating the inventory approach with high-resolution Moderate Resolution Imaging Spectroradiometer (MODIS) active-fire and land cover data, Global Biogeochem. Cy., 20, GB2013, 10.1029/2005gb002547, 2006.

Wang, Q., Itoh, S., Itoh, K., Apaer, P., Chen, Q., Niida, D., Mitsumura, N., Animesh, S., Sekiguchi, K., and Endo, T.: Behavior of suspended particulate matter emitted from combustion of agricultural residue biomass under different temperatures, 1, 3-13, 10.2495/esus130271, 2013.

Wang, Y., Hu, M., Lin, P., Guo, Q., Wu, Z., Li, M., Zeng, L., Song, Y., Zeng, L., Wu, Y., Guo, S., Huang, X., and He, L.: Molecular characterization of nitrogen-containing organic compounds in humic-like substances emitted from straw residue burning, Environ. Sci. Technol., 51, 5951-5961, 10.1021/acs.est.7b00248, 2017.

Washenfelder, R. A., Attwood, A. R., Brock, C. A., Guo, H., Xu, L., Weber, R. J., Ng, N. L., Allen, H. M., Ayres, B. R., Baumann, K., Cohen, R. C., Draper, D. C., Duffey, K. C., Edgerton, E., Fry, J. L., Hu, W. W., Jimenez, J. L., Palm, B. B., Romer, P., Stone, E. A., Wooldridge, P. J., and Brown, S. S.: Biomass burning dominates brown carbon absorption in the rural southeastern United States, Geophys. Res. Lett., 42, 653-664, 10.1002/2014gl062444, 2015.

Wu, G., Wan, X., Gao, S., Fu, P., Yin, Y., Li, G., Zhang, G., Kang, S., Ram, K., and Cong, Z.: Humic-like substances (HULIS) in aerosols of central Tibetan Plateau (Nam Co, 4730 m asl): Abundance, light absorption properties, and sources, Environ. Sci. Technol., 52, 7203-7211, 10.1021/acs.est.8b01251, 2018.

Wu, G., Ram, K., Fu, P., Wang, W., Zhang, Y., Liu, X., Stone, E. A., Pradhan, B. B., Dangol, P. M., Panday, A. K., Wan, X., Bai, Z., Kang, S., Zhang, Q., and Cong, Z.: Water-soluble brown carbon in atmospheric aerosols from Godavari (Nepal), a regional representative of South Asia, Environ. Sci. Technol., 53, 3471-3479, 10.1021/acs.est.9b00596, 2019.

Wu, G., Wan, X., Ram, K., Li, P., Liu, B., Yin, Y., Fu, P., Loewen, M., Gao, S., Kang, S., Kawamura, K., Wang, Y., and Cong, Z.: Light absorption, fluorescence properties and sources of brown carbon aerosols in the Southeast Tibetan Plateau, Environ. Pollut., 257, 113616, 10.1016/j.envpol.2019.113616, 2020.

Xie, M., Hays, M. D., and Holder, A. L.: Light-absorbing organic carbon from prescribed and laboratory biomass burning and gasoline vehicle emissions, Scientific reports, 7, 7318, 10.1038/s41598-017-06981-8, 2017.

Xie, M., Shen, G., Holder, A. L., Hays, M. D., and Jetter, J. J.: Light absorption of organic carbon emitted from burning wood, charcoal, and kerosene in household cookstoves, Environ. Pollut., 240, 60-67, 10.1016/j.envpol.2018.04.085, 2018.

Xie, M., Chen, X., Hays, M. D., and Holder, A. L.: Composition and light absorption of N-containing aromatic compounds in organic aerosols from laboratory biomass burning, Atmos Chem Phys, 19, 2899-2915, 10.5194/acp-19-2899-2019, 2019.

Yan, J., Wang, X., Gong, P., Wang, C., and Cong, Z.: Review of brown carbon aerosols: Recent progress and perspectives, Sci. Total Environ., 634, 1475-1485, 10.1016/j.scitotenv.2018.04.083, 2018.

Zanatta, E. R., Reinehr, T. O., Awadallak, J. A., Kleinübing, S. J., dos Santos, J. B. O., Bariccatti, R. A., Arroyo, P. A., and da Silva, E. A.: Kinetic studies of thermal decomposition of sugarcane bagasse and cassava bagasse, J. Therm. Anal. Calorim., 125, 437-445, 10.1007/s10973-016-5378-x, 2016.

Zhang, G., Li, J., Li, X. D., Xu, Y., Guo, L. L., Tang, J. H., Lee, C. S., Liu, X., and Chen, Y. J.: Impact of anthropogenic emissions and open biomass burning on regional carbonaceous aerosols in South China, Environ. Pollut., 158, 3392-3400, 10.1016/j.envpol.2010.07.036, 2010.

Zhang, X., Lin, Y. H., Surratt, J. D., and Weber, R. J.: Sources, composition and absorption Angstrom exponent of light-absorbing organic components in aerosol extracts from the Los Angeles Basin, Environ. Sci. Technol., 47, 3685-3693, 10.1021/es305047b, 2013.

Zhu, C. S., Cao, J. J., Huang, R. J., Shen, Z. X., Wang, Q. Y., and Zhang, N. N.: Light absorption properties of brown carbon over the southeastern Tibetan Plateau, Sci. Total Environ., 625, 246-251, 10.1016/j.scitotenv.2017.12.183, 2018.

Figures

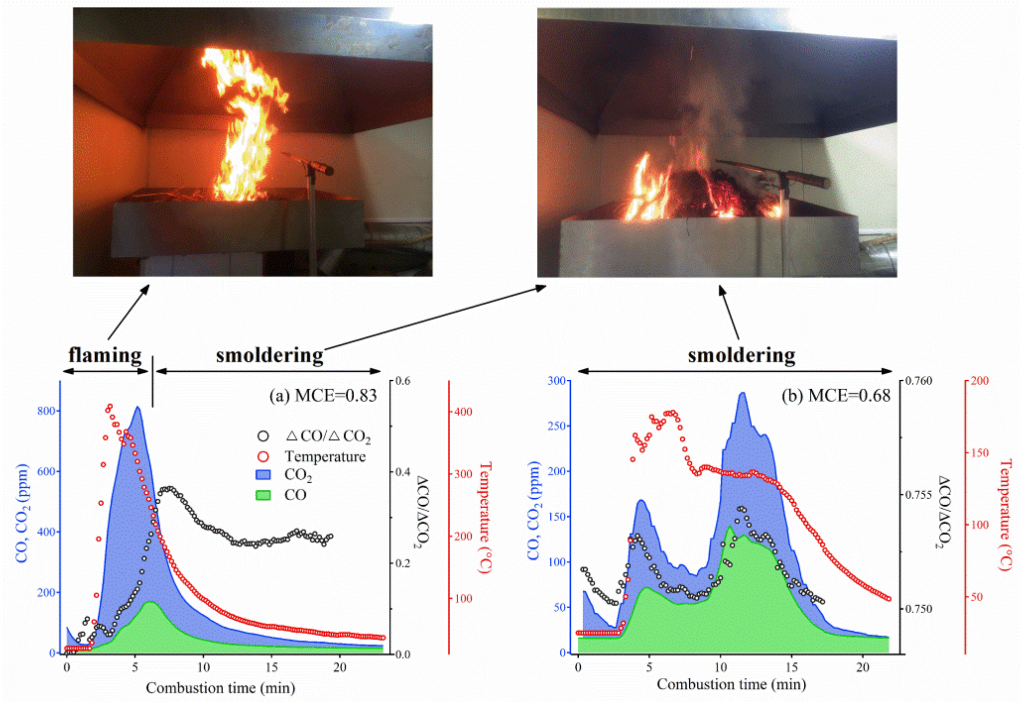

Figure 1 Variations of measured CO, CO_2 concentrations, $\Delta CO/\Delta CO_2$, fire temperatures and burning conditions during two selected experiments, with an averaged MCE value of (a) 0.83 and (b) 0.68.

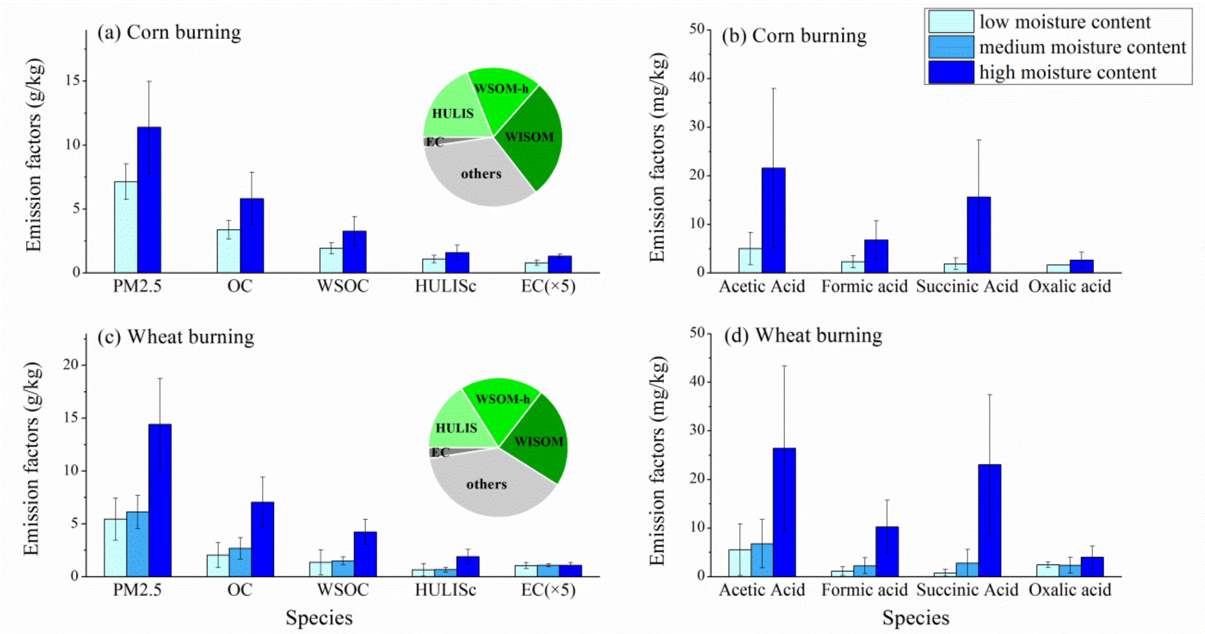

Figure 2 Emission factors of $PM_{2.5}$, OC, WSOC, $HULIS_C$ and EC from (a) corn burning and (c) wheat burning, and emission factors of low molecular weight organic acids (acetic acid, formic acid, succinic acid, and oxalic acid) from (b) corn burning and (d) wheat burning. The EC emission factors are represented by 5×EC due to the low values. The pie charts in panels (a) and (c) represent the contribution of major carbonaceous aerosols among $PM_{2.5}$. The high-polarity WSOM (WSOM-h) is

calculated by subtracting HULIS from WSOM. Different moisture content levels correspond to those shown in Table S1.

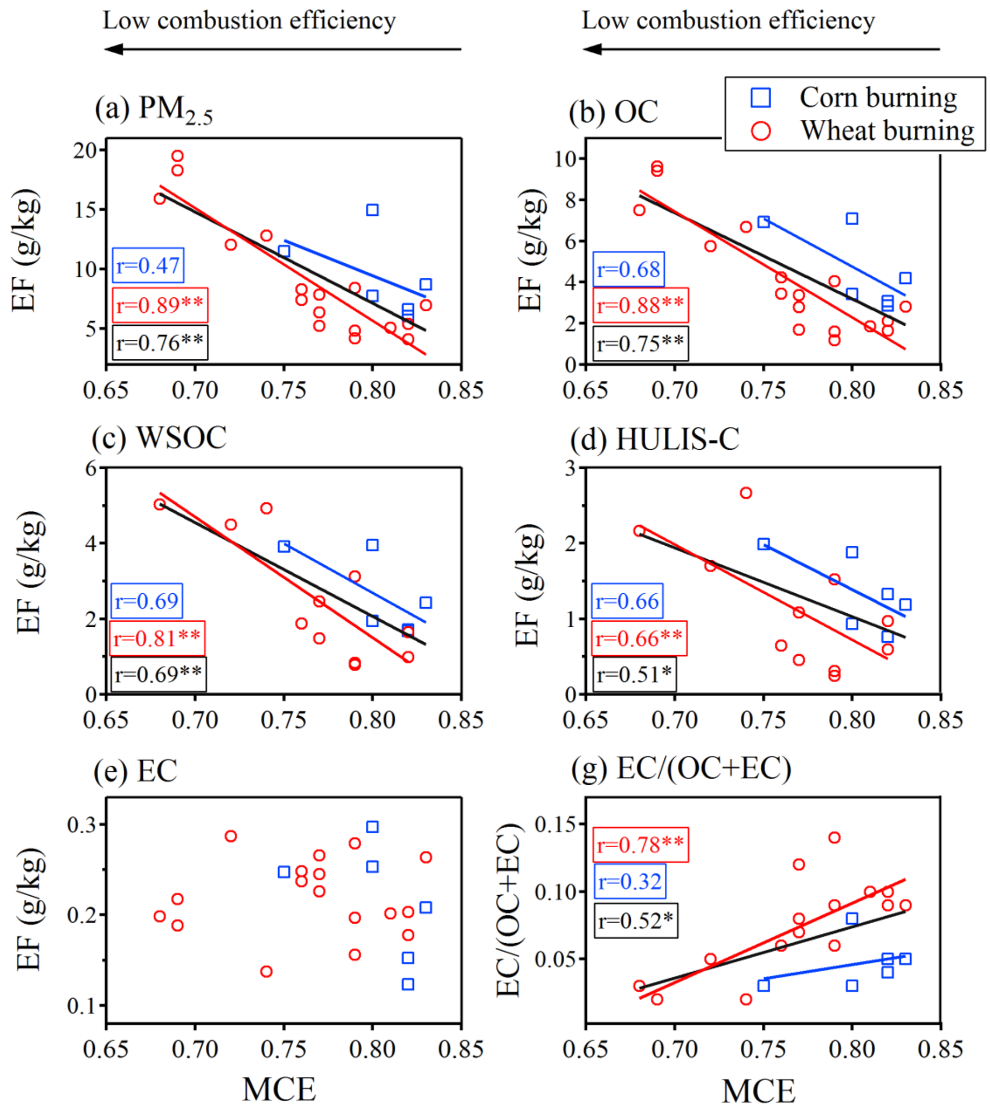

Figure 3 Emission factors of $PM_{2.5}$, carbonaceous aerosols (OC, WSOC, $HULIS_C$ and EC) and EC/(OC+EC) ratios as a function of modified combustion efficiency (MCE). Corn and wheat burning emissions are denoted by red and blue colors, respectively. The r values in each panel are the Pearson correlations between emission factors and MCE for corn (blue), wheat (red) and the overall (black) burning experiments. The ** or * following the r value indicates the correlation is significant at the 0.01 level or 0.05 level (2-tailed).

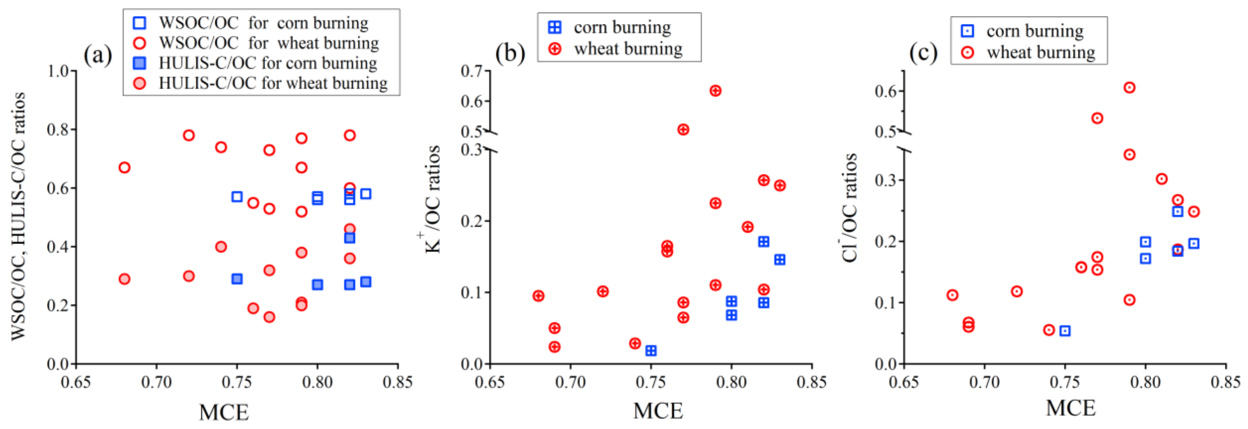

Figure 4 Variations of (a) WSOC/OC and $HULIS_C$/OC ratios, (b) K^+/OC, and (c) Cl^-/OC ratios as a function of modified combustion efficiency (MCE) for corn and wheat burning experiments. Corn and wheat burning emissions are denoted by red and blue colors, respectively.

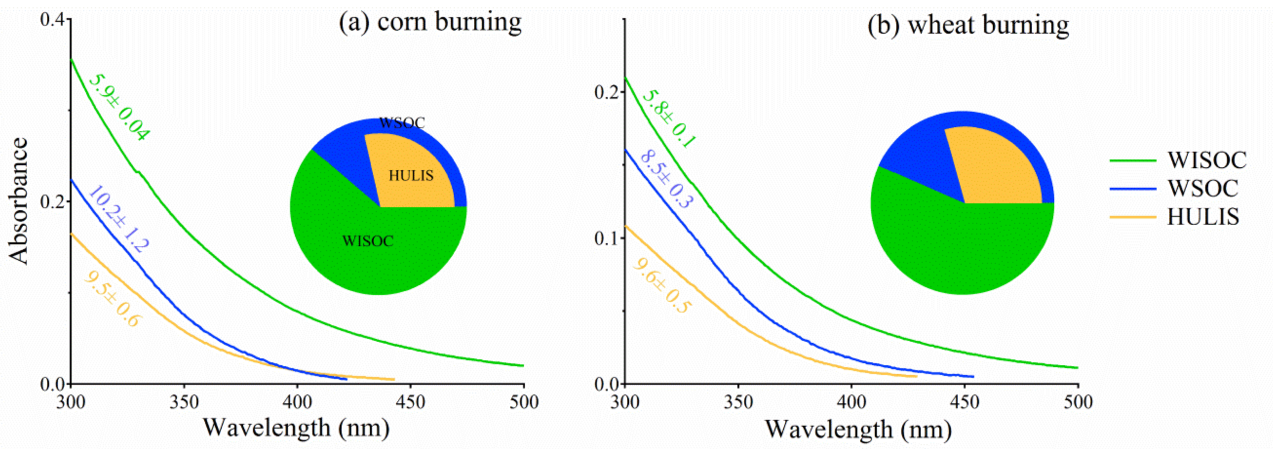

Figure 5 UV-vis spectra of carbonaceous aerosol solutions, including WSOC, $HULIS_C$ and WISOC, from (a) corn and (b) wheat burning experiments. The pie chart in each panel is the absorption contribution of different BBOA fractions at 300 nm. The number represents the average AAE of each BBOA fraction derived from the absorption in the wavelength range of 300-450 nm.

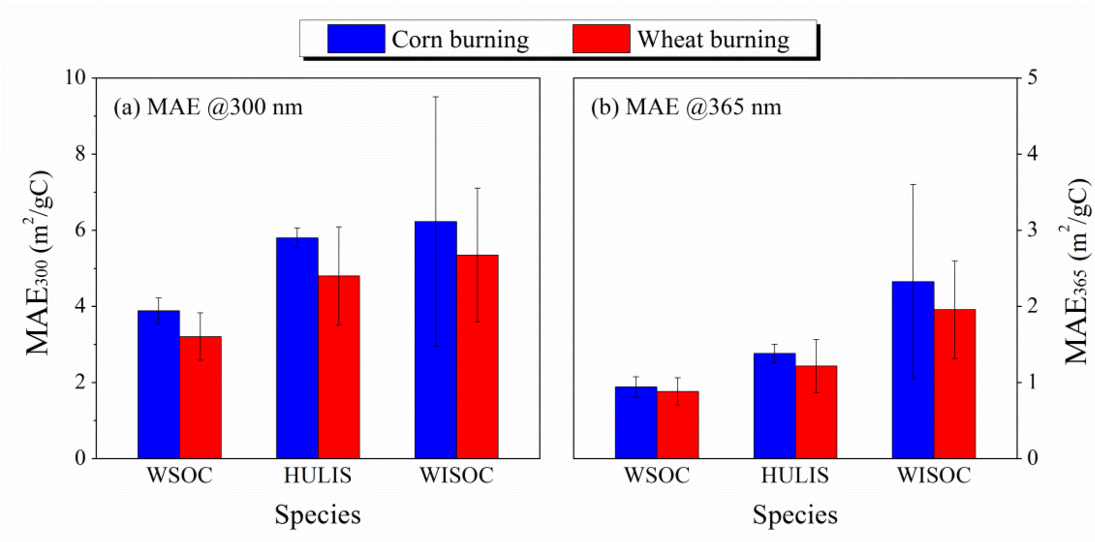

Figure 6 Mass absorption efficiency (MAE) of different organic carbonaceous aerosols, including WSOC, HULIS and WISOC emitted from corn and wheat burning.

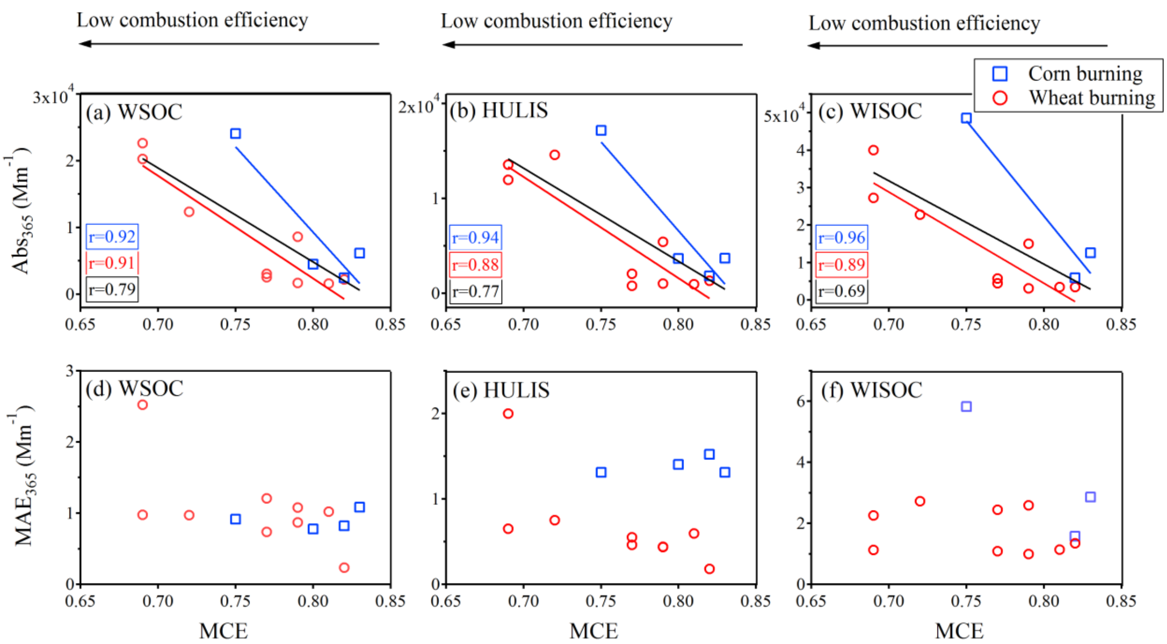

Figure 7 (a-c) Light absorption coefficients (Abs_{365}) and (d-f) mass absorption efficiency (MAE_{365}) of WSOC, $HULIS_C$ and WISOC at 365 nm as a function of combustion efficiency. Corn and wheat burning emissions are denoted by red and blue colors, respectively. The r values in panels (a-c) are the correlation coefficients for corn (blue), wheat (red) and overall (black) burning experiments.

Supplement for

Chemical composition and light absorption of carbonaceous aerosols emitted from crop residue burning: Influence of combustion efficiency

Yujue Wang,[1] Min Hu,[*,1,2,4] Nan Xu,[1] Yanhong Qin,[1] Zhijun Wu,[1,2] Liwu Zeng,[3] Xiaofeng Huang,[3] Lingyan He [3]

[1]State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China

[2]Collaborative Innovation Center of Atmospheric Environment and Equipment Technology, Nanjing University of Information Science & Technology, Nanjing, China

[3]Key Laboratory for Urban Habitat Environmental Science and Technology, School of Environment and Energy, Peking University Shenzhen Graduate School, Shenzhen, China

[4]Beijing Innovation Center for Engineering Sciences and Advanced Technology, Peking University, Beijing 100871, China

Correspondence to: Min Hu (minhu@pku.edu.cn)

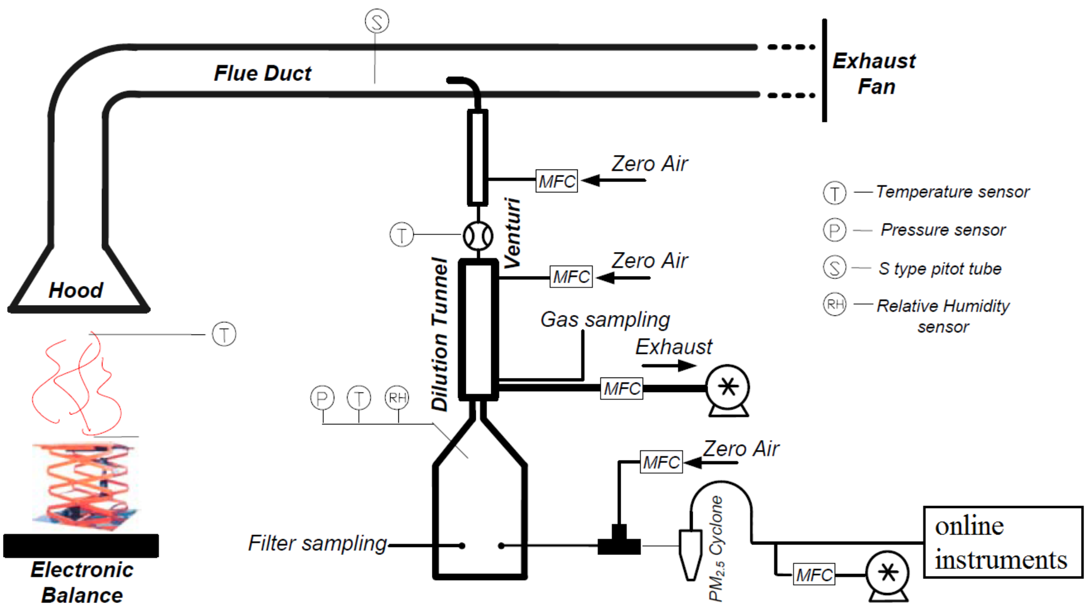

Figure S1 Scheme of the biomass burning simulation system (He et al., 2010).

Table S1 Burning conditions, including biofuel types, moisture contents and modified combustion efficiency (MCE), of simulated biomass burning experiments in this study

Types of biomass fuels	Moisture content		MCE
Corn	low level	13%	0.83
		13%	0.82
		13%	0.82
	high level	18%	0.80
		18%	0.80
		18%	0.75
Wheat	low level	7%	0.77
		7%	0.79
		7%	0.79
		9%	0.83
		9%	0.79
		9%	/
	medium level	18%	0.76
		18%	0.82
		18%	0.82
		22%	0.81
		22%	0.77
		22%	0.76
	high level	27%	0.77
		27%	0.74
		27%	0.69
		33%	0.69
		33%	0.68
		33%	0.72

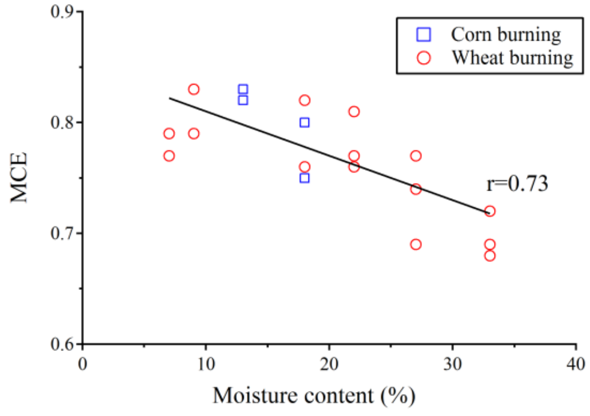

Figure S2 Variations of MCE as a function of moisture contents. The Pearson correlation=0.73 at the 0.01 significance level.

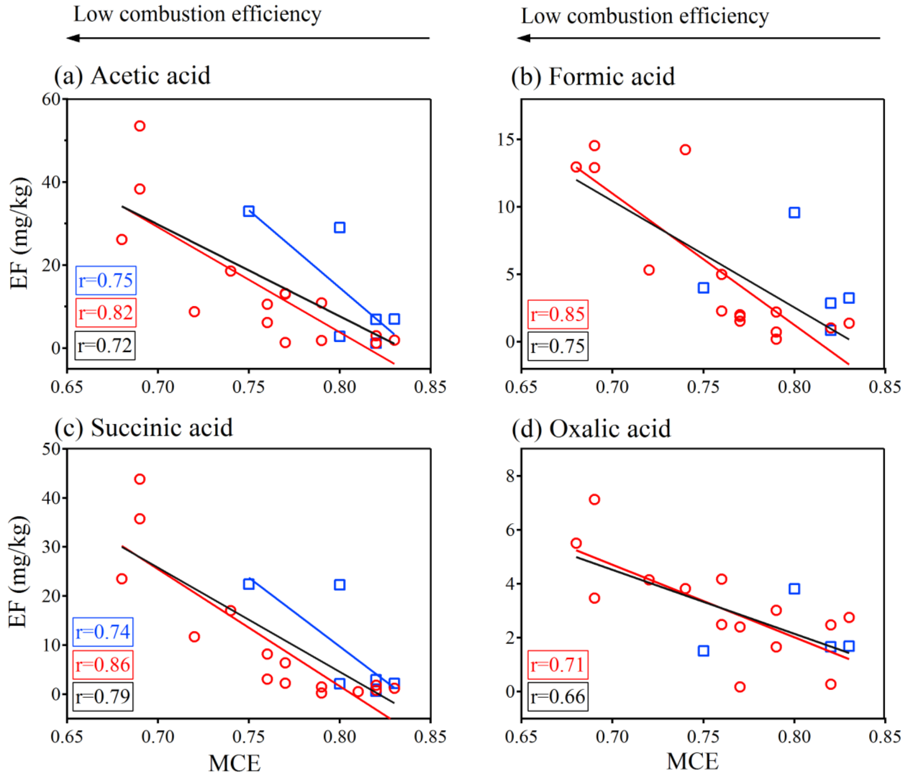

Figure S3 Emission factors of low molecular weight organic acids (acetic acid, formic acid, succinic acid, and oxalic acid) as a function of combustion efficiency. Corn and wheat burning emissions are denoted by red and blue color, respectively. The r values in each panel are the correlation coefficients between emission factors and MCE for corn (blue), wheat (red) and overall (black) burning experiments.

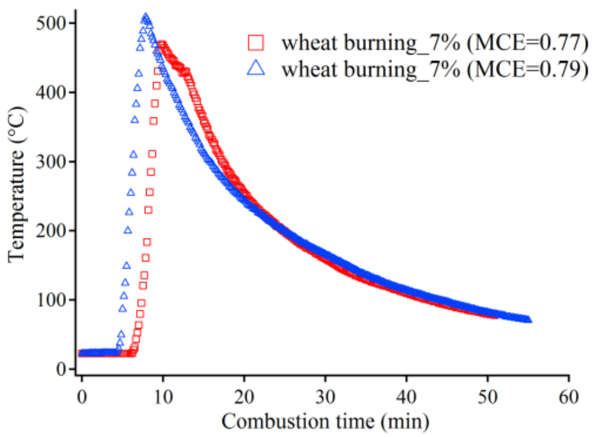

Figure S4 Variations of measured fire temperatures during two wheat straw (moisture content=7%) burning experiments with MCE=0.77 and 0.79.

References

He, L. Y., Lin, Y., Huang, X. F., Guo, S., Xue, L., Su, Q., Hu, M., Luan, S. J., and Zhang, Y. H.: Characterization of high-resolution aerosol mass spectra of primary organic aerosol emissions from Chinese cooking and biomass burning, Atmos. Chem. Phys., 10, 11535-11543, 10.5194/acp-10-11535-2010, 2010.