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Interactive comment on "Comprehensive characterization of humic-like substances in smoke $PM_{2.5}$ emitted from the combustion of biomass materials and fossil fuels" *by* Xingjun Fan et al.

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Interactive comment on "Comprehensive characterization of humic-like substances in smoke PM2.5 emitted from the combustion of biomass materials and fossil fuels" by Xingjun Fan et al.

We are grateful to Anonymous Referee #2 for his/her valuable comments, and have carefully revised our manuscript accordingly. A point-to-point response to this reviewer's comments is given below.

General Comments: This study discusses comprehensive characterization of humi-

clike substances (HULIS) in PM2.5 samples from combustions of biomass materials (rice straw, corn straw, and pine branch) and fossil fuels (lignite coal and diesel fuel), and from ambient air. To achieve the goals of this study, water-soluble HULIS fractions were group isolated using a HLB solid phase extraction method and then quantified with a TOC analyzer. Also chemical properties and structures of HULIS were further investigated using elemental analyzer, UV-vis spectroscopy, excitation-emissions matrix (EEM) fluorescence spectroscopy, FTIR spectroscopy, and 1H-NMR spectroscopy. Characteristics of primary HULIS from biomass burning (BB) and fossil fuel (FF) combustion emissions were compared with the result from ambient samples and with those reported from many previous publications. Results indicate the chemical properties and structures of primary HULIS from combustion emissions of biomass and fossil fuels are very similar to chemical features of ambient HULIS in this and previous studies, which are indicated by a variety of analytical tools, with some distinct differences. It is worthy of note that primary HULIS contain mostly low molecular weight compounds. Results from this study can add to the database of chemical properties and structures for BB and FF-derived HULIS, and thereby contribute to better understanding of the role of BB and FF aerosols in ambient environments. Also this work may help to identify future focus in related to molecular level characterization of ambient brown carbon. However, most of the findings from this study were demonstrated by previous publications. Thus, authors should address the unique scientific finding of this work a bit more in revised manuscript. Overall the manuscript is written well, and with some further explanation of collected data and further elaboration on the results it will be ready for publication. Below are specific revision comments for the authors to consider in their next revision.

Reply: Thanks for the comments. We have carefully revised that and address the unique scientific finding of this work a bit more in revised manuscript. The detailed explanation could be found in our reply to referee #1, #2, and the revised manuscript.

Specific comments:

Abstract section I would suggest adding important quantitative information from the study.

Reply: Thanks. We have added some important quantitative information in revised manuscript. The details are as follows:

Page 1, lines 17-20: "The results show that HULIS account for 11.2–23.4% and 5.3% of PM2.5 emitted from biomass burning (BB) and coal combustion, respectively. In addition, contributions of HULIS-C to total carbon and water soluble carbon in smoke PM2.5 emitted from BB and coal combustion are 8.0–21.7% and 5.2%, 56.9–66.1% and 45.5%, respectively."

Page 2, lines 8-15: "HULIS from coal combustion had a lower O/C molar ratio (0.27), and a higher content of [Ar–H] (31%), suggesting that aromatic compounds were extremely abundant in HULIS from this source. Moreover, the absorption Ångström exponents of primary HULIS from BB and coal combustion were 6.7–8.2 and 13.6, respectively. The mass absorption efficiencies of primary HULIS from BB and coal combustion at 365 nm (MAE365) were 0.97–2.09 and 0.63 m2/gC, respectively. Noticeable higher MAE365 for primary HULIS from BB than coal combustion indicate the former one has stronger contribution to the light absorbing properties of aerosols in atmospheric environment."

1. Introduction section Park and Yu (2016) examined the chemical and light absorption properties of HULIS in PM2.5 from burning of three different types of biomass burning fuels (rice straw, pine needles, and sesame branch) in a laboratory combustion chamber ("Chemical and light absorption properties of humic-like substances from biomass burning emissions under controlled combustion experiments". Atmospheric Environment 136, 114-122). Authors may refer to the paper to compare their results.

Reply: Thanks. This is an excellent paper. We have added this reference and make some comparisons in revised manuscript. The details are as follow:

Page 4, lines 3-12: "On recently study, the chemical and light absorption properties of HULIS in PM2.5 from burning of three different types of biomass burning fuels (rice straw, pine needles, and sesame branch) in a laboratory combustion chamber were investigated by Park and Yu (2016). According to this study, primary HULIS from BB accounted for 15.3–29.5% of PM2.5 emissions, and HULIS-C contributed 15–29% of OC and 36–63% of WSOC, respectively. Although the study brought a better understanding on light absorption properties of primary WSOC from BB, but the observation on the optical and structural features of primary HULIS is limited (Park and Yu, 2016). On the other hand, as important energy resources, fossil fuels (such as coal, diesel fuel) are consumed significantly around the world, and to be important sources of black carbon in ambient aerosols (Cao et al., 2006). However, the content and chemical properties of primary HULIS from fossil fuels combustion are still unknown. "

Page 11, lines 17-21: "It can be seen that the mass of the HULIS fractions accounted for 11.2–23.4% of the PM in smoke PM2.5 emitted from BB, which is comparable to the results (7.6–29.5%) for BB reported in previous studies (Lin, 2010b, Park and Yu, 2016). It is worth noting that the highest HULIS abundance (23.4 $\pm$ 5.5%) was detected in rice straw smoke PM2.5, which is consistent with 29.5% for similar samples observed by Park and Yu (2016)."

Page 12, line 16-line 18: "These results are very consistent with the results reported for BB in previous studies (Schmidl et al., 2008a,b; Goncalves et al., 2010; Lin et al., 2010b; Park and Yu, 2016)."

We also have added some valuable data (red) from this reference in revised Table 2.

The added reference is:

Park, S. S., and Yu, J.: Chemical and light absorption properties of humic-like substances from biomass burning emissions under controlled combustion experiments, Atmos. Environ., 136, 114-122, 10.1016/j.atmosenv.2016.04.022, 2016.

2. Experimental section 2.1. Sampling (pages 4-5) Lines 11-12 on page 4: It is described that "..five types of smoke PM2.5 samples were collected to . . .from the combustion of biomass .." How many sets of PM2.5 samples did you collect for each of biomass types and coal fuel? Need to be added in the revision. Was only one sample used for each burn to investigate the comprehensive characterization of HULIS in smoke aerosols samples? If so, they should describe the reliability and/or uncertainties of the experimental results. Also how many ambient samples did you use to conduct the experiments?

Reply: Thanks for comments. We have added some descriptions on sampling of smoke PM2.5 and ambient PM2.5 in revised manuscript. In the study, five sets of PM2.5 samples were collected for each of biomass types and coal fuel. Then five filters in different sets were chosen from different sets for each type of smoke PM2.5 and ambient PM2.5 and were used to investigate the comprehensive characterization of HULIS. The details of sample number have been also added in the revised Table 2. The sentences have been revised as follow:

Page 6, lines 8-17: "The combustion experiments of biomass fuels (rice straw, corn straw and pine branch) were carried out under open air without any controlled conditions to simulate open burning in the field. Smoke PM2.5 samples were collected on Whatman quartz filters (Ø 90 mm) by two samplers in the chamber. For each biomass combustion experiment, biomass materials were firstly cut into pieces, and then were ignited and burned out, and one set of two smoke PM2.5 filters were collected during whole burning process (5∼15 min). Totally, five sets filter samples were collected for each biomass fuel. The coal combustion was carried out according to the method introduced by Huang et al. (2013). The combustion stove was put into the chamber when the combustion condition was stabled, and then one set of smoke PM2.5 sample was collected for approximately 10 min, and a total of five sets of filter samples were obtained."

Page 6, lines 21-23: "In addition to the smoke PM2.5 samples emitted directly from the

combustion process, ambient PM2.5 samples were also collected during December 7 to 11, 2015 in Wushan, Guangzhou, China. Each sample was collected for approximately 24h, and a total of 5 filters were obtained."

Combustion conditions of three biomass materials and lignite coal in a laboratory resuspension chamber should be described in detail because the burning conditions such as smoldering or flaming burns, combustion temperature, air dilution ratio, flue gas temperature at a sampling location, etc., affect greatly the abundance and chemical properties and structures of WSOC, HULIS, and organic compounds. Also burning conditions might generate water-soluble aerosols of different optical properties. Details in this regard would be helpful. At what stage of the burning were the samples collected? Please be as specific as possible.

Reply: Thanks for comments. This is a good idea, however the smoke PM2.5 samples were collected from uncontrolled combustion in current study. We believed that the studies of HULIS formed from different burning conditions such as smoldering or flaming burns, combustion temperature, air dilution ratio, flue gas temperature at a sampling location, etc. would be very interesting works. Thanks for the advices.

In the current manuscript, we added some descriptions on sampling in the experimental section:

Page 6, line 8-line 17: "The combustion experiments of biomass fuels (rice straw, corn straw and pine branch) were carried out under open air without any controlled conditions to simulate open burning in the field. Smoke PM2.5 samples were collected on Whatman quartz filters (Ø 90 mm) by two samplers in the chamber. For each biomass combustion experiment, biomass materials were firstly cut into pieces, and then were ignited and burned out, and one set of two smoke PM2.5 filters were collected during whole burning process (5∼15 min). Totally, five sets filter samples were collected for each biomass fuel. The coal combustion was carried out according to the method introduced by Huang et al. (2013). The combustion stove was put into the chamber

when the combustion condition was stabled, and then one set of smoke PM2.5 sample was collected for approximately 10 min, and a total of five sets of filter samples were obtained."

What were the moisture contents of the biomass burning and coal fuels? The authors need to describe the elemental composition (C, H, O, N, and S) of burning fuels if possible, but for comparison with other papers moisture content would be very helpful.

Reply: Thanks. We have revised the manuscript according to the comments and added the moisture contents, elemental composition (C, H, O, N, and S) of burning fuels in revised manuscripts.

Page 5, line 20- Page 6, line 4: "The biomass materials including rice straw, corn straw, pine branch were collected from rural area of Guangdong province, and the coal (RO = 0.77%) were obtained from Ping Ding Shan, China. The detail information of this type of coal could be found in Huang et al. (2013). The ultimate properties of the three biomass materials and coal are shown in Table 1. On an air-dry basis, moisture content measured for the rice straw, corn straw, pine branch and coal was 5.8 $\pm$ 0.5, 7.4 $\pm$ 0.8, 7.6 $\pm$ 0.7, and 1.6 $\pm$ 0.2 %, respectively. Carbon (C), hydrogen (H), and oxygen (O) contents were found to range from 36.0 to 72.6%, 4.0 to 7.2%, and 8.2 to 45.0% for combustion materials, respectively. In comparison with biomass materials, coal substantially comprised of higher C content (72.6%) and lower O content (8.2%). There were no significant differences among biomass materials in terms of elemental compositions."

Moreover, the moisture contents, elemental compositions (C, H, O, N, and S) of burning fuels also have been added in a new Table 1 in current manuscript.

Please add collection time for biomass smokes.

Reply: The collection time is not fixed at a constant time. For each BB combustion experiment, the sampling was conducted until it burned out (5-15 min). The combustion

experiment of coal was conducted according to the method introduced by Huang et al. (2013), and one set of smoke PM2.5 samples was collected for approximately 10 min after the combustion condition was stabled. The sentence has been revised as follow:

Page 6, line 11-line 17: "For each biomass combustion experiment, biomass materials were firstly cut into pieces, and then were ignited and burned out, and one set of two smoke PM2.5 filters were collected during whole burning process (5$\sim$15 min). Totally, five sets filter samples were collected for each biomass fuel. The coal combustion was carried out according to the method introduced by Huang et al. (2013). The combustion stove was put into the chamber when the combustion condition was stabled, and then one set of smoke PM2.5 sample was collected for approximately 10 min, and a total of five sets of filter samples were obtained."

2.2. Isolation of HULIS Lines 5-6 on page 6: ". . .more filters were used to obtain HULIS for the analysis of the elemental composition. . ." Instead of using the HULIS samples re-dissolved in 20 mL Milli-Q water (section 2.2), new filter samples were used for further analyses? More detailed description would be helpful for readers.

Reply: No. The "more filters were used to obtain HULIS for the analysis of the elemental composition. . ." are not the new filter samples. They are a part remainder of filters that have been measured for the quantification of HULIS. We have revised that as follow:

Page 7, line 16-line 18: "Moreover, more area of the corresponding filters was used to obtain enough dried HULIS for the analysis of the elemental composition, as well as FTIR and 1H NMR spectrometry."

2.3.2. Elemental composition Lines 20-21 on page 6: "A portion of the HULIS (redissolved in methanol) was transferred into . . .." The HULIS eluate used in this analysis was not re-dissolved in water? How much volume of MeOH did you use for this?

Reply: In the study, the HULIS was evaporated to dryness under a gentle nitrogen stream. However, the resulting dried HULIS were not fully in the form of solid powder, but viscous substances. This dried HULIS sample can't be re-dissolved in pure water. Therefore, the HULIS samples were re-dissolved in methanol for elemental analysis in the study. The operate procedure are as follow:

In the experiment, the HULIS sample was re-dissolved them in 3 mL of methanol, then one or two droplets (~1 mg dried HULIS) was transferred into to a pre-cleaned tin capsule of known weight and dried under vacuum. The mass of the dried HULIS in the tin capsule was determined using a micro balance and then the elemental composition was determined by the elemental analyzer.

2.3.6. 1H-NMR spectroscopy "About 10 mg of dried HULIS were re-dissolved in 1 mL of MeOD." could be changed to ". . ..of MeOH."

Reply: We have revised the sentence as follow:

Page 11, lines 6-7: "About 10 mg of dried HULIS were dissolved in deuterated methanol (MeOH-d4, 1 mL) and transferred to 5 mm NMR tubes."

3. Results and discussion 3.1. The abundance of HULIS in smoke PM2.5 and ambient PM2.5 These results should be compared with those from Park and Yu (2016). In Table 1, please include number of samples used in the experiments for each of BB, FF, and ambient samples. References of Park et al. in Table 1 are not listed in the list of the references.

Reply: Thanks. We have revised the manuscript according to the comments. The details are as follow:

Page 11, lines 19-21: "It is worth noting that the highest HULIS abundance (23.4 ± 5.5%) was detected in rice straw smoke PM2.5, which is consistent with 29.5% for similar samples observed by Park and Yu (2016)."

Page 12, lines 16-18: "These results are very consistent with the results reported for BB in previous studies (Schmidl et al., 2008a, b; Goncalves et al., 2010; Lin et al.,

2010b; Park and Yu, 2016)."

In addition, we have added the number of samples used in the experiments for each of BB, FF, and ambient samples in revised Table 2 (i.e., the old Table 1), and also added some valuable data from Park and Yu (2016) in revised Table 2 (i.e., the old Table 1).

Finally, the references of "References of Park et al. in Table 1" have been added in revised manuscript:

Page 33, Lines 22-24: Park, S. S., Cho, S. Y., Kim, K. W., Lee, K. H., and Jung, K.: Investigation of organic aerosol sources using fractionated water-soluble organic carbon measured at an urban site, Atmos. Environ., 55, 64-72, DOI 10.1016/j.atmosenv.2012.03.018, 2012.

Page 33, Lines 25-26: Park, S. S., and Cho, S. Y.: Characterization of Organic Aerosol Particles Observed during Asian Dust Events in Spring 2010, Aerosol Air Qual. Res., 13, 1019-1033, DOI 10.4209/aaqr.2012.06.0142, 2013.

Page 33, Lines 27-28: Park, S. S., Schauer, J. J., and Cho, S. Y.: Sources and their contribution to two water-soluble organic carbon fractions at a roadway site, Atmos. Environ., 77, 348-357, DOI 10.1016/j.atmosenv.2013.05.032, 2013.

Page 33, Lines 29-30: Park, S. S., and Yu, J.: Chemical and light absorption properties of humic-like substances from biomass burning emissions under controlled combustion experiments, Atmos. Environ., 136, 114-122, 10.1016/j.atmosenv.2016.04.022, 2016.

3.2. Elemental composition Lines 15-21 on page 11: In Table 2, OM/OC ratios for four types of primary HULIS are presented. They did not measure OC concentration. Details how OM/OC ratios got determined from elemental composition data should described in the text.

Reply: Thanks. We have added a description for the OM/OC determination in Table 3 of revised manuscript.

In the study, OM/OC represents the organic matter-to-organic carbon mass ratio. The OM is referred to the mass of HULIS, which has been determined with microbalance. The OC is referred to mass of carbon content of HULIS, which has been measured with elemental analyzer. Finally, the OM/OC ratio was calculated from the mass ratio of OM to OC.

3.3 UV-vis properties & 3.4 Fluorescence properties I think that authors measured light absorption spectra of WSOC and HULIS from BB, FF, and ambient samples. I would suggest providing absorption angstrom exponents (AAE) and mass absorption efficiencies (MAE) of samples from burning of different types of biomass and coal fuels, and ambient environment. These information could be much useful for understanding light absorption characteristics and radiative forcing effects by BB and coal burning derived brown carbon aerosols.

Reply: Thanks for the comments. We have added the discussion of AAE and MAE of HULIS samples from burning of different types of biomass and coal fuel, and from ambient aerosols in revised manuscript. We clearly stated in our revised manuscript as below:

Page 2, lines 10-15: "Moreover, the absorption Ångström exponents of primary HULIS from BB and coal combustion were 6.7–8.2 and 13.6, respectively. The mass absorption efficiencies of primary HULIS from BB and coal combustion at 365 nm (MAE365) were 0.97–2.09 and 0.63 m2/gC, respectively. Noticeable higher MAE365 for primary HULIS from BB than coal combustion indicate the former one has stronger contribution to the light absorbing properties of aerosols in atmospheric environment."

Page 9, line 21- Page 10, line 12: a new section of "(3) Light absorption properties . . .." was added in the experimental section of revised manuscript.

Page 24, line 22- Page 26, line 12: A new section of "3.7 Light absorption properties" was added in the results and discussion section in revised manuscript.

Page 27, lines 8-9: "The AAE and MAE365 of the BB derived primary HULIS were similar to those of atmospheric HULIS and/or WSOM."

Page 28, lines 1-3: "The MAE365 of BB HULIS are 0.97-2.09 m2/g, which are higher than that of coal combustion HULIS, suggesting the former one own stronger light absorption properties."

We also added a new Table 7 "Summary of AAE and MAE365 of HULIS and WSOM" in revised manuscript.

Moreover, some new references have been also added in revised manuscript. (Page 29, lines 26-27; Page 29, lines 28-30; Page 29, lines 31-Page 30, line 1; Page 30, lines 26-28; Page 32, lines 5-7; Page 32, lines 8-9; Page 32, lines 15-17; Page 32, lines 18-20; Page 33, lines 1-3; Page 33, lines 29-30; Page 35, lines 12-14; Page 35, lines 15-17)

Lines 19-20 on page 13 and lines 10-11 on page 15. Authors stated that based on the SUVA254 values from primary smoke HULUS, "the primary HULIS contained higher aromatic degree and/or higher MW compounds", but results from EEM spectra indicate that "primary HULIS contain mostly low MW compounds". This means that primary HULIS from BB and FF smokes contain both high and low MW compounds? Further elaboration on this is needed.

Reply: Thanks. In order to avoid the misunderstanding, these sentences are revised as follows:

Page 16, lines 22-24: "These results indicate that the primary HULIS contain more aromatic groups with conjugation of π-bonds alongside aliphatic structures."

Page 18, lines 17-20: "This finding indicates that these four types of primary HULIS are consist of more phenol-like, protein-like, and/or aromatic amino acids than atmospheric HULIS (Coble, 1996; Peuravuori et al., 2002; Duarte et al., 2004; Kieber et al., 2006)."

3.7 Comparison pf primary HULIS and 4 Conclusions Sections 3.7.1, 3.7.2, and 3.7.3

are very similar to the explanations in sections 3.2-3.6, so it needs to be condensed, or I suggest combining the section 3.7 with section 4. Conclusions.

Reply: Thanks for the comments. This is a good idea. We have revised that in current manuscript. The section 3.7 has been combined with section 4. Conclusions in revised manuscript. The revisions are as follow:

Page 26, line 14-page 28, line 6: “4. Conclusions. . .. . .” in revised manuscript

4. Conclusions It will be much more valuable if a paragraph was added to conclusions describing what the authors think was important and how it can be applied

Reply: We have added a new paragraph to introduce the implication in revised manuscript. The revisions are as follow:

Page 28, lines 8-Page 29, line 1: “5 Implications. . .. . ..” was added in revised manuscript.

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