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Atmospheric Chemistry and Physics Discussions

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.

Anonymous Referee #2

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General Comments: This study discusses comprehensive characterization of humic-like 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) com-

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bustion 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.

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

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.

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 sam-

ple 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?

Combustion conditions of three biomass materials and lignite coal in a laboratory re-suspension 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.

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.

Please add collection time for biomass smokes.

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.

2.3.2. Elemental composition Lines 20-21 on page 6: "A portion of the HULIS (re-dissolved 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?

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."

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.

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.

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.

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.

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.

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.

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