

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 PM_{2.5} emitted from the combustion of biomass materials and fossil fuels” by Xingjun Fan et al.

Dear AC Duarte,

Thanks for your interests and helpful comments in our paper. We have carefully revised the manuscript according to the comments. A point-to-point response to the comments is given below. We hope we answered your questions adequately.

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1. General comments

This comprehensive characterization of humic-like substances (HULIS) in smoke PM_{2.5} emitted from the combustion of biomass materials and fossil fuels becomes a highly recommendable work for publication since it is really “comprehensive” by using several spectroscopies besides elemental analysis. The authors avoid the discussion WSOC vs HULIS vs. WSOM (water soluble organic matter) although the filter samples were ultrasonically extracted with Milli-Q water, the water soluble extracts were filtered, the filtrate was adjusted to a pH value of 2, and finally introduced in a SPE (Oasis HLB) cartridge. When comparing this HULIS isolation procedure with the WSOM isolation procedure suggested by (Duarte and Duarte, 2005) a comment should be made regarding the operational definition of HULIS as different sorbents extract different organic moieties as already shown exactly by the authors of this submitted paper for discussion (Fan et al., 2013).

Reply: Thanks for the comments. We have added some operational definitions and comments when comparing this HULIS isolation procedure with the WSOM isolation procedure suggested by (Duarte and Duarte, 2005) and others in revised manuscript. In addition, the HULIS isolation procedures have been added in the Table 2, 3 and 4 of the revised manuscript. The revisions stated in our revised manuscript are as below:

Page 3, lines 9-10: “Their carbon (C) mass accounts for 9%–72% of the C content of water soluble organic matter (WSOM) in atmospheric aerosols (Feczko et al., 2007; Krivacsy et al., 2008; Lin et al., 2010b; Fan et al., 2012; Song et al., 2012).”

Page 3, line 20- Page 4, line 1: “HULIS fractions have been found in smoke particles emitted from the combustion of wood and leaves, the carbon content of HULIS (HULIS-C) make up 0.6–21.2% of the total mass of particles (Schmidl et al., 2008a; Schmidl et al., 2008b; Goncalves et al., 2010). HULIS accounted for 7.6–12.4% of the particle mass, and HULIS-C contributed approximate 14.3–14.7% and 30–33% of the organic carbon (OC) and the water soluble carbon (WSOC), respectively.”

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Moreover, a comment regarding the operational definition of HULIS has been added. The revisions are as follow:

Page 7, lines 19- Page 8, lines 1: "It is noted that the eluates here represent the hydrophobic portion of WSOM and were named as water soluble HULIS. According to the literatures (Graber and Rudich, 2006; Zheng et al., 2013), these water soluble hydrophobic WSOM can be isolated with different SPE methods. In spite of some differences were observed among of them, these hydrophobic WSOM isolated with different sorbents are very similar in chemical compositions and properties according to our previous studies (Fan et al., 2012, 2013). Therefore, for better comparison with other studies, the hydrophobic WSOM isolated by SPE methods (i.e. HLB, C-18, DEAE, XAD-8) and other protocols (i.e. ELSD) are all termed as HULIS in this paper."

The variety of materials studied, biomass materials (rice straw, corn straw, and pine branch) and fossil fuels (lignite coal and diesel fuel) allow substantiating the discussion and reach quite accurate and meaningful conclusions regarding the characterization of HULIS from biomass burning (BB) and HULIS from coal combustion. Furthermore, in addition to the smoke PM_{2.5} samples from the BB and fuel combustion, ambient PM_{2.5} samples were also collected during December, 2015, which allowed the authors to discuss similarities and differences between primary HULIS and atmospheric HULIS. Regarding the use of UV-Vis, fluorescence and ¹H-NMR spectroscopies for the characterization of properties of HULIS from atmospheric aerosols there are very recent references that also shed some light on this matter and they should be considered when discussing the results of the submitted paper. For the case UV-Vis spectroscopy there is a reference (Matos et al., 2015b) where the authors used comprehensive two-dimensional liquid chromatography (LCxLC) coupled with a diode array detector (DAD) in order to assessing the chemical heterogeneity and mapping the hydrophobicity vs. molecular weight distribution of the most hydrophobic acid fractions in WSOC (which the authors consider as water soluble organic matter, WSOM) from fine atmospheric aerosols collected over different seasons at a urban location. For the case

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of fluorescence spectroscopy there are two important recent references (Matos et al., 2015a; Paula et al., 2016). In the first reference (Matos et al., 2015a) the authors combine fluorescence datasets of excitation-emission matrices (EEM) fluorescence spectra and Parallel Factor Model (PARAFAC) with Alternating Least Squares (ALS) algorithm in order to further compare sets of excitation-emission matrices fluorescence spectra of WSOC and Alkaline Soluble Organic Carbon (ASOC), sequentially extracted from urban aerosols collected during different seasons. In the reference (Paula et al., 2016) the authors use a comprehensive multidimensional analysis approach for exploiting simultaneously the compositional changes over a molecular size continuum and associated light-absorption (ultraviolet absorbance and fluorescence) properties of WSOM and alkaline soluble organic matter (ASOM), sequentially extracted from urban aerosols collected during different seasons. For the case of ¹H-NMR spectroscopy there are the following two references: a) (Lopes et al., 2015) where the authors applied ¹H NMR spectroscopy to characterize the structural features of WSOC and ASOC, sequentially extracted, from fine urban atmospheric aerosols collected over different seasons, and further assess their sources through the pre-established ¹H NMR source apportionment fingerprinting approach; and b) (Duarte et al., 2008) where the authors applied 2D NMR techniques to deliver new qualitative information on the substructures present in water soluble organic matter from fine rural atmospheric aerosols. Furthermore the following reference (Duarte and Duarte, 2015) should also be considered as an appropriate background on the application of NMR spectroscopy for acquiring detailed structural characterization of the complex natural organic matter contained in atmospheric aerosols.

Reply: Thanks a lot. We have revised the text according to the comments and added some recent references when discussing the results in revised manuscript. The revisions stated in our revised manuscript are as below:

Page 16, lines 22- Page 17, lines 2: "These results indicate that the primary HULIS contain more aromatic groups with conjugation of π -bonds alongside aliphatic struc-

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tures. Similar characters were also found in many previous studies. For example, it has been found that HULIS fraction in colder season presented more aromatic structures than those in warmer season, of which the BB might be an important contribution of the former one (Baduel et al., 2010; Matos et al., 2015a, b; Paula et al., 2016).”

Page 20, lines 7-9: “The bands at 1458 and 1610 cm⁻¹, which are generally attributed to the C–C stretching of aromatic rings (Watanabe and Kuwatsuka, 1992; Duarte et al., 2015), are observed in spectra of primary HULIS from direct combustion emissions.”

Page 21, lines 15-18: “A critical review on the application of ¹H NMR spectroscopy on WSOM in atmospheric aerosols has been presented, in which ¹H NMR was demonstrated to be an important and novel tool to characterize WSOM, which can not only provide deeply insight into the structural characteristics of them but also reflect their sources (Duarte and Duarte, 2015).”

Page 21, lines 22- Page 22, lines 1: “The four types of primary HULIS displayed similar spectra to the atmospheric HULIS spectra in this study, which were also comparable to ¹H NMR spectra of HULIS and/or WSOM in fog (Decesari et al., 2000), cloud (Decesari et al., 2005), rain water (Santos et al., 2009, 2012), biomass burning aerosols (Graham et al., 2002) and urban/rural aerosol (Decesari et al., 2007; Ziemba et al., 2011; Song et al., 2012; Fan et al., 2013; Lopes et al., 2015).”

Page 22, lines 9-11: “Among these sharp signals, a limited number of resonances could be attributed to specific organic species by comparison with previous studies (Decesari et al., 2000, 2001; Suzuki et al., 2001; Matta et al., 2003; Cavalli et al., 2006; Chalbot et al., 2014, 2016; Lopes et al., 2015)”

Page 22, line 24-Page 23, line 4: “This suggests that HULIS consists of a complex mixture of organic substances (Samburova et al., 2007; Song et al., 2012; Fan et al., 2013; Lopes et al., 2015). The integrated ¹H NMR signal over specific ranges of chemical shift has been used previously to quantify the contribution of organic functional groups in HULIS from urban/rural aerosols (Song et al., 2012; Fan et al., 2013; Lopes et al.,

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2015) and rainwater (Miller et al., 2009; Santos et al., 2009, 2012).”

Page 23, lines 18-24: “These four functional groups have also been observed in the ¹H NMR spectra of atmospheric HULIS in this and other studies, but the relative distribution of these four functional groups are different. Whether atmospheric HULIS in this work or in other studies from ambient aerosol (Song et al., 2012; Fan et al., 2013; Lopes et al., 2015) and rainwater (Miller et al., 2009; Santos et al., 2009, 2012) were all characterized by a predominance of [R-H] (37–60%), followed by [H–C–C=] (20–37%) and [H–C–O] (10–24%), and a less contribution from [Ar–H] (1–12%).”

Page 24, Line 2-4: “This result is also consistent with the observations of more aromatic protons in HULIS in colder seasons ascribed to BB influence (Song et al., 2012; Lopes et al., 2015).”

We also added more information (red) in Table 6 in revised manuscript.

Some new references have been added in revised manuscript:

Duarte, R. M., and Duarte, A. C.: Unraveling the structural features of organic aerosols by NMR spectroscopy: a review, *Magn Reson Chem*, 53, 658-666, 10.1002/mrc.4227, 2015.

Duarte, R. M. B. O., Freire, S. M. S. C., and Duarte, A. C.: Investigating the water-soluble organic functionality of urban aerosols using two-dimensional correlation of solid-state ¹³C NMR and FTIR spectral data, *Atmos. Environ.*, 116, 245-252, 10.1016/j.atmosenv.2015.06.043, 2015.

Lopes, S. P., Matos, J. T. V., Silva, A. M. S., Duarte, A. C., and Duarte, R. M. B. O.: ¹H NMR studies of water- and alkaline-soluble organic matter from fine urban atmospheric aerosols, *Atmos. Environ.*, 119, 374-380, 10.1016/j.atmosenv.2015.08.072, 2015.

Matos, J. T. V., Freire, S. M. S. C., Duarte, R. M. B. O., and Duarte, A. C.: Natural organic matter in urban aerosols: Comparison between water and alkaline soluble components using excitation–emission matrix fluores-

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cence spectroscopy and multiway data analysis, *Atmos. Environ.*, 102, 1-10, <http://dx.doi.org/10.1016/j.atmosenv.2014.11.042>, 2015a.

Matos, J. T. V., Freire, S. M. S. C., Duarte, R. M. B. O., and Duarte, A. C.: Profiling Water-Soluble Organic Matter from Urban Aerosols Using Comprehensive Two-Dimensional Liquid Chromatography, *Aerosol Sci. Technol.*, 49, 381-389, 10.1080/02786826.2015.1036394, 2015b.

Paula, A. S., Matos, J. T., Duarte, R. M., and Duarte, A. C.: Two chemically distinct light-absorbing pools of urban organic aerosols: A comprehensive multidimensional analysis of trends, *Chemosphere*, 145, 215-223, 10.1016/j.chemosphere.2015.11.093, 2016.

Finally, the reference (Duarte et al., 2015) should also be taken into account when interpreting the structural features of HULIS from the acquired FTIR spectra (section 3.5). In this reference, the authors used two-dimensional (2D) correlation spectroscopy, applied to one-dimensional solid-state cross polarization magic angle spinning (CP-MAS) ¹³C NMR, FTIR, and the combination of CP-MAS ¹³C NMR and FTIR data, to glean new structural information on the most hydrophobic water soluble organic matter (WSOM) from fine urban air particles collected during different seasons.

Reply: Thanks. We have revised the text when interpreting the structural features of HULIS from the acquired FTIR spectra and added this reference in revised manuscript. The details are as below:

Page 19, lines 11-13: "As shown in Figure 3, the spectra of primary HULIS were similar to those of the atmospheric HULIS and WSOM in this and previous studies (Havers et al., 1998; Krivacsy et al., 2001; Kiss et al., 2002; Duarte et al., 2005; Polidori et al., 2008; Santos et al., 2009; Fan et al., 2013; Duarte et al., 2015)."

Page 20, line 1-3: "These FTIR spectra features are similar to those of the atmospheric HULIS described in this and other studies (Krivacsy et al., 2001; Duarte et al., 2005;

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Song et al., 2012; Fan et al., 2013; Duarte et al., 2015)."

Page 20, lines 5-9: "Relative weaker band at 1710 cm⁻¹ for primary HULIS than for atmospheric HULIS was observed in Figure 3, indicating the former ones present less carboxyl groups (Song et al., 2012; Fan et al., 2013). The bands at 1458 and 1610 cm⁻¹, which are generally attributed to the C–C stretching of aromatic rings (Watanabe and Kuwatsuka, 1992; Duarte et al., 2015), are observed in spectra of primary HULIS from direct combustion emissions."

The reference has been added in revised manuscript:

Duarte, R. M. B. O., Freire, S. M. S. C., and Duarte, A. C.: Investigating the water-soluble organic functionality of urban aerosols using two-dimensional correlation of solid-state ¹³C NMR and FTIR spectral data, *Atmos. Environ.*, 116, 245-252, 10.1016/j.atmosenv.2015.06.043, 2015.

All in all, the results add up to an already extensive data set of characteristics of WSOM of aerosols but this work brings an original and comprehensive comparison between excellent proxies for primary HULIS representing biomass burning and fossil fuel combustion and ambient air samples analyzed by several spectroscopies. Therefore the differences found between primary and atmospheric HULIS as well as the differences found among the four types of primary HULIS can be considered well validated and this study contributes to a better understanding of the differences in chemical nature of primary HULIS from direct combustion emissions and their contribution to atmospheric HULIS.

2. Specific comments

The Abstract should contain more quantitative data and instead of sentences like "HULIS accounted for a significant proportion of the particle matter, . . ." (line 17, page 1) the figures resulting from thus study should be included.

Reply: Thanks. We have revised the abstract according to the comments and more

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quantitative data were included in the abstract.

Page 1, lines 17-20: "The results show that HULIS account for 11.2–23.7% and 5.3% of PM_{2.5} emitted from biomass burning (BB) and coal combustion, respectively. In addition, contributions of HULIS-C to total carbon and water soluble carbon in smoke PM_{2.5} emitted from BB and coal combustion are 8.0–21.7% and 5.2%, 56.9–66.1% and 45.5%, respectively."

There should be a clarification of the terms HULIS, WSOC and WSOM and not only of HULIS as mentioned in page 2, lines 17 and 18, WSOC as mentioned in page 3, lines 3 and 4.

Reply: Thanks for the comments. We have added the definitions of HULIS, WSOC and WSOM and made a clarification of the terms HULIS, WSOC and WSOM in revised manuscript. The details are as follows:

Page 3, lines 9-11: "Their carbon (C) mass accounts for 9%–72% of the C content of water soluble organic matter (WSOM) in atmospheric aerosols (Feczko et al., 2007; Krivacsy et al., 2008; Lin et al., 2010b; Fan et al., 2012; Song et al., 2012)"

Page 3, lines 20-22: "HULIS fractions have been found in smoke particles emitted from the combustion of wood and leaves, the carbon content of HULIS (HULIS-C) make up 0.6–21.2% of the total mass of particles (Schmidl et al., 2008a; Schmidl et al., 2008b; Goncalves et al., 2010)"

Page 3, line 22-Page 4, line 1: "HULIS have also been found to be abundant in fresh burning emissions from rice straw and sugar cane leaves (Lin et al., 2010a; Lin et al., 2010b). HULIS accounted for 7.6–12.4% of the particle mass, and HULIS-C contributed approximate 14.3–14.7% and 30–33% of the organic carbon (OC) and the water soluble carbon (WSOC), respectively."

Page 7, line 19- Page 8, line 1: "It is noted that the eluates here represent the hydrophobic portion of WSOM and were named as water soluble HULIS. According to

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the literatures (Graber and Rudich, 2006; Zheng et al., 2013), these water soluble hydrophobic WSOM can be isolated with different SPE methods. In spite of some differences were observed among of them, these hydrophobic WSOM isolated with different sorbents are very similar in chemical compositions and properties according to our previous studies (Fan et al., 2012, 2013). Therefore, for better comparison with other studies, the hydrophobic WSOM isolated by SPE methods (i.e. HLB, C-18, DEAE, XAD-8) and other protocols (i.e. ELSD) are all termed as HULIS in this paper."

Moreover, the HULIS isolation procedures have been also added in the revised Table 2, 3 and 4.

Furthermore, in page 9, lines 21-23, the authors perform an estimate of the contribution of the so-called HULIS to WSOC, using TOC and UV-vis absorbance at 250 nm (UV₂₅₀) measurements. While the use of TOC is most appropriate for such a comparison, additional details on the use of UV₂₅₀ measurements should be provided, namely if the UV data were normalized to the amount of carbon of each sample/fraction. This is important for the sake of easier comparison between HULIS and WSOC fractions, mostly because HULIS is an isolated/concentrated fraction of WSOC and it is enriched in those organic moieties preferably retained by the SPE sorbent.

Reply: Thanks for the comments. We have added some details on the use of UV₂₅₀ measurements in the revised manuscript. In the study, the UV₂₅₀ measurement was used to investigate the contribution of HULIS fraction in total WSOM. The UV data weren't normalized to the amount of carbon of each sample/fraction. The details are as below:

Page 9, lines 9-15: "As demonstrated by many studies, the high absorbing UV chromophoric compounds (strong absorbing at 250 nm) are major components in WSOM, which usually tended to be enriched in the SPE isolated HULIS fractions (Baduel et al., 2009; Fan et al., 2012, 2013, 2016; Song et al., 2012; Duarte et al., 2015; Lopes et al., 2015; Fan et al., 2016). Therefore, the ratio between the UV₂₅₀ of HULIS and original

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WSOM has been widely used to evaluate the relative contribution of HULIS to WSOM in terms of chromophoric compounds content. It should be noted that HULIS solution must keep the same volume to original WSOM solution for the UV250 determination.”

In page 8, line 21 there is the following text “The abundance of HULIS in rice straw smoke PM2.5 ($10.7 \pm 0.8\%$). . .” but according to Table 1, this value is for the urban PM2.5 samples and not for rice straw smoke PM2.5. Please correct this inconsistency.

Reply: I am sorry for this mistake. The sentence has been revised as follow:

Page 11, lines 23-25: “The abundance of HULIS in rice straw smoke PM2.5 ($23.4 \pm 5.5\%$) was also significantly higher than in ambient PM2.5 in this study, and in some previous studies (as listed in Table 2).”

In page 11, lines 18 to 21, the lower OM/OC ratio reported also suggests that primary HULIS in coal smoke are less oxidized than those of HULIS in BB smoke PM2.5. It is difficult to assess the degree of unsaturated components on the basis of the elemental composition data.

Reply: Thanks. We have revised the statement and revised the sentences in revised manuscript.

Page 15, lines 2-5: “The HULIS samples in the three types of biomass smoke PM2.5 had a relatively lower C content (52.9–57.4%), higher O content (33.0–38.3%), higher O/C molar ratio (0.43–0.54) and higher OM/OC (1.74–1.89) than those in coal smoke PM2.5. These results indicated that the HULIS in BB smoke contained a relatively higher content of O-containing components.”

Besides, no discussion is found regarding the elemental analysis data (including atomic ratios and OM/OC ratio) of the collected ambient HULIS. For this sample, the values depicted in Table 1 are different from those reported for primary HULIS. A discussion on these differences and values should be included in the manuscript.

Reply: Thanks. We have added some discussions for the elemental analysis data of

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the collected ambient HULIS in revised manuscript.

Page 13, lines 22-25: “It is obvious that the primary HULIS contain substantially higher C and lower O than ambient HULIS in this study. However, these results are comparable with those for atmospheric HULIS in previous studies (Krivacsy et al., 2001; Kiss et al., 2002; Duarte et al., 2007; Salma et al., 2007; Song et al., 2012; Fan et al., 2013; Duarte et al., 2015).”

Page 14, lines 8-12: “Among the four types of primary HULIS, the O/C ratios of the three types from BB were in the range of 0.43–0.54, which were lower than 0.65 for ambient HULIS in this study, but were comparable with data (0.30–0.76) for atmospheric HULIS reported in previous studies (Krivacsy et al., 2001; Kiss et al., 2002; Duarte et al., 2007; Salma et al., 2007; Song et al., 2012; Fan et al., 2013).”

Page 14, lines 15-24: “The H/C molar ratios of the four primary types of HULIS were in the ranges of 1.15 to 1.43, which were lower than that (1.59) for atmospheric HULIS in this work. However, they dropped in the range of observations (1.01–1.53) reported in previous studies (Krivacsy et al., 2001; Kiss et al., 2002; Duarte et al., 2007, 2015; Salma et al., 2007; Song et al., 2012; Fan et al., 2013). The N/C molar ratios of primary HULIS were 0.03–0.06, with both being similar to the results for atmospheric HULIS in this and previous studies (Table 3). In addition, the ratio of OM to organic C (OM/OC) mass ratios of the four types of primary HULIS ranged from 1.51 to 1.89, which were lower than 2.06 for ambient HULIS in this study, but were generally in the range of the data (1.5–2.28) reported for atmospheric HULIS in previous studies (Krivacsy et al., 2001; Kiss et al., 2002; Duarte et al., 2007; Salma et al., 2007; Song et al., 2012; Fan et al., 2013; Duarte et al., 2015).”

The sentence in page 12, lines 2 to 4 (“In contrast, the HULIS in coal smoke had a relatively lower content of O-containing components and a higher content of unsaturated structures.”) should be deleted since it is not adding any new valuable information into the discussion.

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Reply: Thanks. We have deleted it.

In page 18, lines 17 to 19: the authors should identify these signals (“sharp peaks”) in their ¹H NMR spectra in Figure 4. This will be most helpful for readers not familiarized with the interpretation of NMR data. An additional remark on this issue: the identification of single compounds in complex NMR spectra, such as those of Figure 4, is highly arguable. Therefore, the authors should also make this comment in the discussion.

Reply: Thanks. We have added some comments for these signals in the discussion. The paragraph has been revised as follow:

Page 22, lines 11-22: “These sharp signals included low molecular weight formate (δ 8.44 ppm), terephthalic acid (δ 8.01 and 8.12 ppm), phthalic acid (δ 7.45–7.47 and 7.58 ppm), glucose (δ 3.88–3.91 and 3.81–3.85 ppm), fructose (δ 3.79–3.84 ppm), trimethylamine (δ 2.71 and 2.89 ppm), dimethylamine (δ 2.72 ppm), monomethylamine (δ 2.55 ppm). It is worth noting that all BB-derived HULIS present more sharp glucose and fructose resonances than atmospheric HULIS in ¹H NMR spectra, but they were absent for coal combustion derived HULIS. On the other hand, coal combustion derived HULIS contain more sharp resonances of terephthalic acid and phthalic acid than atmospheric HULIS, but they were absent for BB-derived HULIS. Moreover, whether BB-derived or coal combustion derived HULIS exhibit many sharp signals between 6.5–8.5 ppm, which could ascribed to aromatic structures, such as substituted phenols and alkylbenzenes (around 6.6–7.0 ppm), benzoic acids, esters, and nitroaromatics (Suzuki et al., 2001; Chalbot et al., 2014).”

We have also revised the Figure 4, and given some identifications for some sharp peaks in the revised Figure 4 in current manuscript.

In page 20, paragraph in lines 1 to 5: A more in-depth comparison should be made between NMR data obtained for primary and ambient HULIS.

Reply: Thanks. We have made a more in-depth comparison between NMR data ob-

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tained for primary and ambient HULIS in revised manuscript:

Page 23, line 18-page 24, line 4: “These four functional groups have also been observed in the ¹H NMR spectra of atmospheric HULIS in this and other studies, but the relative distribution of these four functional groups are different. Whether atmospheric HULIS in this work or in other studies from ambient aerosol (Song et al., 2012; Fan et al., 2013; Lopes et al., 2015) and rainwater (Miller et al., 2009; Santos et al., 2009, 2012) were all characterized by a predominance of [H–C] (37–60%), followed by [H–C–C=] (20–37%) and [H–C–O] (10–24%), and a less contribution from [Ar–H] (1–12%). It was noted that the relative content of [Ar–H] groups (19–31%) in primary HULIS was significantly higher than that in atmospheric HULIS. This suggests that primary HULIS contained more aromatic structures, which is consistent with the elemental composition, UV-vis spectra, EEM fluorescence spectra, and FTIR spectra results. This result is also consistent with the observations of more aromatic protons in HULIS in colder seasons ascribed to BB influence (Song et al., 2012; Lopes et al., 2015).”

In page 20, line 10: Please, be aware that this group [H–C–C=] is more likely to have contributions from carbonyl groups (C=O) than from aromatic carbons. Please, consult the original reference (Decesari et al., 2007) for the approach adopted in order to distinguish between these two contributions.

Reply: Thanks. We have revised that in current manuscript.

Page 24, lines 6-9: “As shown in Table 6, there was a relatively higher content of [H–C–C=] (40%) and [Ar–H] (31%) in primary HULIS from coal combustion than from BB, indicating that the primary HULIS in coal smoke contained more unsaturated aliphatic (i.e., carbonyl groups (C=O)) and aromatic structural groups.”

Page 24, line 16-line 20: “For the HULIS from BB, a relatively high content of [C–H] and low content of [Ar–H] were observed for HULIS from pine branch combustion when compared to the HULIS from rice straw and corn straw combustion. These results suggest that the primary HULIS from pine branch combustion contained relative higher

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content of aliphatic protons and lower content of aromatic protons than the HULIS from rice straw and corn straw combustion.”

In page 22, paragraph in lines 5 and 6 (“The similarities between 5 primary and atmospheric HULIS suggest they have similar chemical compositions and properties”): at least, this means that they share similar proton functional groups; however, they differ in terms of their relative distribution among the different samples.

Reply: Thanks. This is an inexact conclusion. So we have deleted this sentence in revised manuscript.

3. References

Decesari, S., Mircea, M., Cavalli, F., Fuzzi, S., Moretti, F., Tagliavini, E. and Facchini, M. C.: Source Attribution of Water-Soluble Organic Aerosol by Nuclear Magnetic Resonance Spectroscopy, *Environ. Sci. Technol.*, 41(7), 2479–2484, doi:10.1021/es061711l, 2007.

Duarte, R. M. B. O. and Duarte, A. C.: Application of Non-Ionic Solid Sorbents (XAD Resins) for the Isolation and Fractionation of Water-Soluble Organic Compounds from Atmospheric Aerosols, *J. Atmos. Chem.*, 51(1), 79–93, doi:10.1007/s10874-005-8091-x, 2005.

Duarte, R. M. B. O. and Duarte, A. C.: Unraveling the structural features of organic aerosols by NMR spectroscopy: a review, *Magn. Reson. Chem.*, 53(9), 658–666, doi:10.1002/mrc.4227, 2015.

Duarte, R. M. B. O., Silva, A. M. S. and Duarte, A. C.: Two-Dimensional NMR Studies of Water-Soluble Organic Matter in Atmospheric Aerosols, *Environ. Sci. Technol.*, 42(22), 8224–8230, doi:10.1021/es801298s, 2008.

Duarte, R. M. B. O., Freire, S. M. S. C. and Duarte, A. C.: Investigating the watersoluble organic functionality of urban aerosols using two-dimensional correlation of solid-state ¹³C NMR and FTIR spectral data, *Atmos. Environ.*, 116, 245–252,

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doi:10.1016/j.atmosenv.2015.06.043, 2015.

Fan, X., Song, J. and Peng, P.: Comparative study for separation of atmospheric humic-like substance (HULIS) by ENVI-18, HLB, XAD-8 and DEAE sorbents: Elemental composition, FT-IR, ¹H NMR and off-line thermochemolysis with tetramethylammonium hydroxide (TMAH), *Chemosphere*, 93(9), 1710–1719, doi:10.1016/j.chemosphere.2013.05.045, 2013.

Lopes, S. P., Matos, J. T. V., Silva, A. M. S., Duarte, A. C. and Duarte, R. M. B. O.: ¹H NMR studies of water- and alkaline-soluble organic matter from fine urban atmospheric aerosols, *Atmos. Environ.*, 119, 374–380, doi:10.1016/j.atmosenv.2015.08.072, 2015.

Matos, J. T. V., Freire, S. M. S. C., Duarte, R. M. B. O. and Duarte, A. C.: Natural organic matter in urban aerosols: Comparison between water and alkaline soluble components using excitation–emission matrix fluorescence spectroscopy and multiway data analysis, *Atmos. Environ.*, 102, 1–10, doi:10.1016/j.atmosenv.2014.11.042, 2015a.

Matos, J. T. V., Freire, S. M. S. C., Duarte, R. M. B. O. and Duarte, A. C.: Profiling Water-Soluble Organic Matter from Urban Aerosols Using Comprehensive Two-Dimensional Liquid Chromatography, *Aerosol Sci. Technol.*, 49(6), 381–389, doi:10.1080/02786826.2015.1036394, 2015b.

Paula, A. S., Matos, J. T. V., Duarte, R. M. B. O. and Duarte, A. C.: Two chemically distinct light-absorbing pools of urban organic aerosols: A comprehensive multidimensional analysis of trends, *Chemosphere*, 145, 215–223, doi:10.1016/j.chemosphere.2015.11.093, 2016.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, doi:10.5194/acp-2016-397, 2016.