

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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Received and published: 17 June 2016

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,

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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).

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 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

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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. 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.

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

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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 this study should be included.

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. 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.

In page 8, line 21 there is the following text “The abundance of HULIS in rice straw smoke PM_{2.5} (10.7 ± 0.8%) . . .” but according to Table 1, this value is for the urban PM_{2.5} samples and not for rice straw smoke PM_{2.5}. Please correct this inconsistency.

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 PM_{2.5}. It is difficult to assess the degree of unsaturated components on the basis of the elemental composition data. Besides, no discussion is found regarding the elemental analysis

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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.

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.

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.

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.

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.

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.

3. References

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