

## **Response to Review Comments (acpd -14-23913-2014)**

### **Response to comments by Anonymous Referee #2**

This manuscript presents the analysis of HULIS and other air pollutants in the samples collected at the Pearl River Delta (China). The authors provide quantitative analysis of WSOC, OC, HULIS, WISOC, different organic and inorganic tracers in the PM 2.5. PMF analysis was applied to estimate the contribution of different sources to the collected samples. This paper is well written and very interesting. It provides an important information on possible sources (e.g. biomass burning) of HULIS. There are several major and minor comments:

Major comments:

1. The author used 1.9 factor to calculate HULIS concentration in  $\mu\text{g C m}^{-3}$  (or HULIS-C). More information is needed how this factor was calculated and why exactly 1.9 was used. Did Lin et al. analyzed similar samples?

**Response:** Referee #1 also raised this question. The same response is copied below.

HULIS-C is calculated from HULIS by assuming a mass-to-carbon ratio of 1.9. The HULIS mass-to-carbon ratio, as determined in a few studies, is quite stable. For example, Kiss et al (2002) they measured elemental composition of the HULIS using an elemental analyzer. They found that HULIS mass-to-carbon ratio was 1.93 and this value was stable throughout their sampling period. In Lin et al (2010), the HULIS mass-to-carbon ratio of some PM<sub>2.5</sub> ambient samples in PRD region was determined to be  $1.94 \pm 0.11$ . In comparison, the conversion ratio of water-soluble organic matter-to-WSOC is not known due to a lack of analytical methods measuring the total water-soluble organic matter. Using HULIS-C allows the easy derivation of WSOC<sub>h</sub> data from WSOC and HULIS<sub>C</sub> and subsequently the investigation of WSOC<sub>h</sub> sources. The following text is added to the revised paper to explain the use of HULIS-C:

“Using HULIS-C allows the easy derivation of WSOC<sub>h</sub> data from WSOC and HULIS<sub>C</sub> and subsequently the investigation of WSOC<sub>h</sub> sources.”

2. It's shown that biomass burning is one of the main sources of HULIS in the collected samples. The author also observed high concentration of HULIS during the summer (June), when biomass burning emissions were low. Secondary processes are mentioned as possible sources of HULIS. It's not clear what kind of secondary processes caused HULIS formation at this area. What are possible precursors that could cause high concentration of HULIS during the summer sampling period?

**Response:** The following text is added to the revised paper to address the questions on the secondary processes and potential precursors for the secondarily formed HULIS.

“Several secondary formation processes, such as aqueous-phase oxidation and heterogeneous reactions, have been demonstrated in laboratory or smog chamber studies to produce HULIS (e.g., Hoffer et al., 2004; Holmes and Petrucci, 2006; Surratt et al, 2008). Sulfation processes involving heterogeneous reactions of oxidation products of biogenic volatile organic compounds (BVOCs) (e.g., isoprene,  $\alpha$ -pinene,  $\beta$ -pinene, and limonene, etc) with sulfate

aerosol have been shown in both chamber and field studies to form organosulfates e.g., Surratt et al., 2008), which are an important class of compounds in the HULIS fraction (e.g., Lin et al., 2012b). Both sulfate aerosol and BVOCs are abundant in PRD, a subtropical and economically more developed region in China. The higher emissions of BVOCs in summer could possibly contribute to the higher HULIS concentrations in this season. In addition to organosulfates, numerous other oxygenated or nitrated organic compound formulas are reported to be HULIS constituents (Lin et al., 2012a), but their formation processes or precursors are much less understood.”

#### References:

Hoffer, A., Kiss, G., Blazso, M., Gelencser, A.: Chemical characterization of humic-like substances (HULIS) formed from a lignin-type precursor in model cloud water. *Geophys. Res. Lett.*, 31, L06115, doi:10.1029/2003GL018962, 2004.

Holmes, B. J., Petrucci, G. A.: Water-soluble oligomer formation from acid-catalyzed reactions of levoglucosan in proxies of atmospheric aqueous aerosols. *Environ. Sci. Technol.* 40, 4983–4989, 2006.

Surratt, J. D., Gómez-González, Y., Chan, A. W., Vermeylen, R., Shahgholi, M., Kleindienst, T. E., Seinfeld, J. H.: Organosulfate formation in biogenic secondary organic aerosol, *J. Phys. Chem. A*, 112, 8345-8378, 2008.

Lin, P., Rincon, A.G., Kalberer, M., Yu, J.Z.: Elemental Composition of HULIS in the Pearl River Delta Region, China: Results Inferred from Positive and Negative Electrospray High Resolution Mass Spectrometric Data, *Environ. Sci. Technol.*, 46, 7454-7462, doi:10.1021/es300285d, 2012a.

Lin, P., Yu, J.Z., Engling, G., Kalberer, M.: Organosulfates in humic-like substance fraction isolated from aerosols at seven locations in East Asia: A study by ultrahigh resolution mass spectrometry. *Environ. Sci. Technol.* 46, 13118-13127, 2012b.

3. Table 1 shows that WISOC fraction is more than half of the total OC. How would the author explain that concentration of WISOC fraction is higher than WSOC, especially when secondary processes were important contributors to HULIS formation (when more oxygenated compounds formed)? More discussions and comparisons with other studies are needed.

**Response:** We do not think there is contradiction in the WISOC, WSOC, and HULIS data. OC consists of WSOC and WISOC if OC is binned according to water-solubility of its constituents. The WSOC fraction is further separated into HULIS (hydrophobic part) and WSOC\_h (hydrophilic part). As we have shown in section 3.2.4, the sources of HULIS and WISOC are different. Secondary processes were important contributors to HULIS, but WISOC could have sources other than secondary source.

#### Minor comments:

Abstract. Line 10. For consistency use “K+” and change “sulfate” and “ammonium” on (SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup>) (see 2.2 “Chemical analysis”, line 2) Introduction. Line 9. Delete “the pure”. SPE does not usually have 100% separation efficiency of organic fraction from inorganic ions.

**Response:** (1) We would still use K rather than K+ in abstract, since element K measured by XRF

was used as PMF inputs because of better accuracy than ionic  $K^+$  measured using the IC system.

(2) “sulfate” and “ammonium” in abstract are changed to  $SO_4^{2-}$  and  $NH_4^+$  as suggested.

(3) Introduction, Line 9, is revised to: “The advantage of SPE is the removal of inorganic ions and the collection of the organic fraction...”

Introduction. Lines 21-22. Reference is needed.

**Response:** The references of redox-reactivity of HULIS are given at the end of the next sentence.

Aerosol sampling. Line 16. “SASS” abbreviation has to be in brackets. Use “medium volume sampler” not “mid-volume sampler”. Line 24. Use comma before “and”

**Response:** Corrected.

Chemical analysis. Line 13. How the extraction was done? Were the filters soaked or sonicated? What kind of instrument was used to get ultrapure water (company, city, country)? Line 25. Add more information how HULIS were isolated using SPE (how cartridges were prepared, how many ml of solvents were used, etc.).

**Response:**

Line 13: Suggestion taken. The sentence is revised as the following:

“For the analysis of WSOC and HULIS, portions of the quartz filters were extracted by sonication in ultrapure water ( $>18M\Omega\cdot cm$ , Barnstead NANOpure ultrapure water system, APS Water Services Corp., USA) with the ratio of 1 mL water per  $1cm^2$  filter.”

Line 25: The method of HULIS isolation using SPE is as the following:

“Briefly, the aerosol water extract was acidified with HCl to  $pH\approx 2$ , then loaded to the SPE cartridge (Oasis HLB,  $30\ \mu m$ , 60 mg/cartridge, Waters, USA). HULIS was retained on the SPE cartridge while the majority of inorganic ions, low molecular weight organic acids, and sugars were not retained. The sorbent was rinsed with 2 mL ultrapure water, and HULIS fraction was then eluted from the SPE cartridge with 1.5 mL methanol containing 2% (w/w)  $NH_3$ . The HULIS eluate was evaporated to dryness under a gentle stream of nitrogen gas and re-dissolved in 1.0 mL of water, followed by detection using an evaporative light scattering detector (ELSD).”

Information on standards is totally missing in the Experimental section (company, city, country).

**Response:** Suggestion taken. The information on standards is added to the manuscript.

Brief description of the TD-GC/MS analysis is needed (instrument, column, etc.). What was the efficiency of the TD-GC/MS analysis?

**Response:** The information about the TD-GC/MS instrument and column used is added in the section 2.2. The method details and evaluation through comparison with the conventional solvent extraction-GC/MS approach have been described in our previous papers. The method evaluation results indicate that the TD-GC/MS method report comparable concentrations to those by the solvent extraction approach for the target non-polar organic compounds.

The following text is added to section 2.2

“The experimental details and method evaluation through comparison with solvent extraction GC-MS analysis are described in our previous papers (Ho and Yu, 2004; Ho et al., 2008).”

#23923. Line 10. Use “obvious” or “noticeable” not “excellent” before “correlations”

**Response:** Corrected.

#23928. Line 9. Use reference available for a reader

**Response:** There is no published reference on HULIS from coal combustion.

#23929. Line 19. Use WISOC not “water-insoluble OC” for consistency.

**Response:** Corrected.