Point-to-point response to Review Comments (acpd -14-23913-2014)

Anonymous Referee #1

General comments: This manuscript presents novel insight to the sources of HULIS in the atmosphere through a thoughtful analysis of HULIS, carbon fractions, elements, and organic species and positive matrix factorization (PMF). The methods used are of high scientific quality and are clearly described.This study provides a thorough and meaningful quantitative analysis of the sources of HULIS, which has not previously been accomplished with the level of detail and rigor shown here. The results are significant, in that they provide quantitative source apportionment of HULIS-C and other carbon fractions to major source categories in the PRD region. The presentation quality could be improved, and clarifications and further discussion of certain points are needed as outlined below.

Specific comments:
1. The observation of HULIS in the ship emission factor is surprising and a novel finding of this paper. The authors need to address the possibility that this HULIS could be associated with secondary processing of this source rather than primary emissions. The PMF model will include both primary and secondary sources in this factor if they sufficiently co-vary. The presence of secondary inorganic ions (e.g. sulfate and ammonium) suggests that some of the primary emissions have been processed.

Response: Yes, in the source profile, some ammonium and sulfate appear in the ship emission factor. While we cannot entirely exclude the possibility that some of the primary ship emissions have been processed, sulfate (and ammonium through its close chemical association with sulfate) could be a primary emission product of residue oil combustion due to its sulfur content. The following text is added to the revised paper for clarification of the ship emission factor:

> Lines 428-431:
> “We note that some sulfate appears in the ship emission source factor. This could be a result of primary emissions from sulfur-containing fuel constituents in the residue oil or that some of the primary ship emissions have been processed. As such, HULIS in the ship emission factor could be partly secondary products of ship emissions atmospheric aging.”

2. The ship contribution to Hulis C, WSOC-H, WSOC, and WISOC does not appear to vary with wind direction. Why? It would expectedly be greater in marine air masses, so it is surprising that it is not.

Response: At the NS site, ship contributions to Hulis-C, WSOC_h, WSOC, and WISOC do not appear to vary with wind direction. This reflects that ship emissions are a local source to NS as the NS site is quite near the NS port (15 km away). In comparison, in GZ the contributions are higher on “Marine” days. GZ site is ~50 km north from NS port, and thus when air mass is from the marine, ship contribution to GZ increases.

3. Alkanes and PAH were measured, but ambient concentrations are neither discussed nor included in the source apportionment model. Perhaps it is best to

Response: The PAH and alkanes are not specific tracers. For example, PAHs are from multiple sources. Therefore, we did not include them in the PMF. As the focus of this paper is on HULIS, we feel the discussion of ambient concentrations of alkanes and PAHs is not essential.

4. Please clarify what PM2.5 component was set as the master variable in PMF modeling. I could reasonably assume PM2.5 or HULIS-C, but cannot discern from the text.

Response: HULIS-C is the focus of our PMF analysis.

5. Page 23918, line 5: Provide the rationale for including HULIS-C in the PMF model rather than HULIS mass.

Response: For source apportionment of HULIS by PMF, either HULIS or HULIS-C can be used without influencing the source apportionment results. 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 $PM_{2.5}$ ambient samples in PRD region was determined to be 1.94±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_h data from WSOC and HULIS_C and subsequently the investigation of WSOC_h sources. The following text is added to the revised paper to explain the use of HULIS-C:

> Lines 137-139:
> "Using HULIS-C allows the easy derivation of WSOC_h data from WSOC and HULIS_C and subsequently the investigation of WSOC_h sources."

6. Section 3.1.1. should briefly discuss the PM mass loadings observed in this study, their seasonal variation, and comparison to prior studies in the region.

Response: The following text is added in Section 3.1.1, and the following figure (Figure R1) was added into the supplementary materials (Figure S5).

> "Annual average $PM_{2.5}$ concentration was higher in GZ (56 $\mu g/m^3$) than NS (44 $\mu g/m^3$) during this study period. They were lower than measurements obtained for the period of July 2007-August 2008 (GZ: 78 $\mu g/m^3$, NS: 66 $\mu g/m^3$) (Lin et al., 2010b). Seasonally, $PM_{2.5}$ was higher in winter (GZ: 68$\mu g/m^3$, NS: 57$\mu g/m^3$) than summer (GZ: 39$\mu g/m^3$, NS: 25$\mu g/m^3$) (Fig. S5). Sulfate and organic matter (OM) were the two most abundant components. OM accounted for 1/4 to 1/3 of $PM_{2.5}$ mass in summer and winter (Fig. S5), indicating the importance of sources analysis of OM."

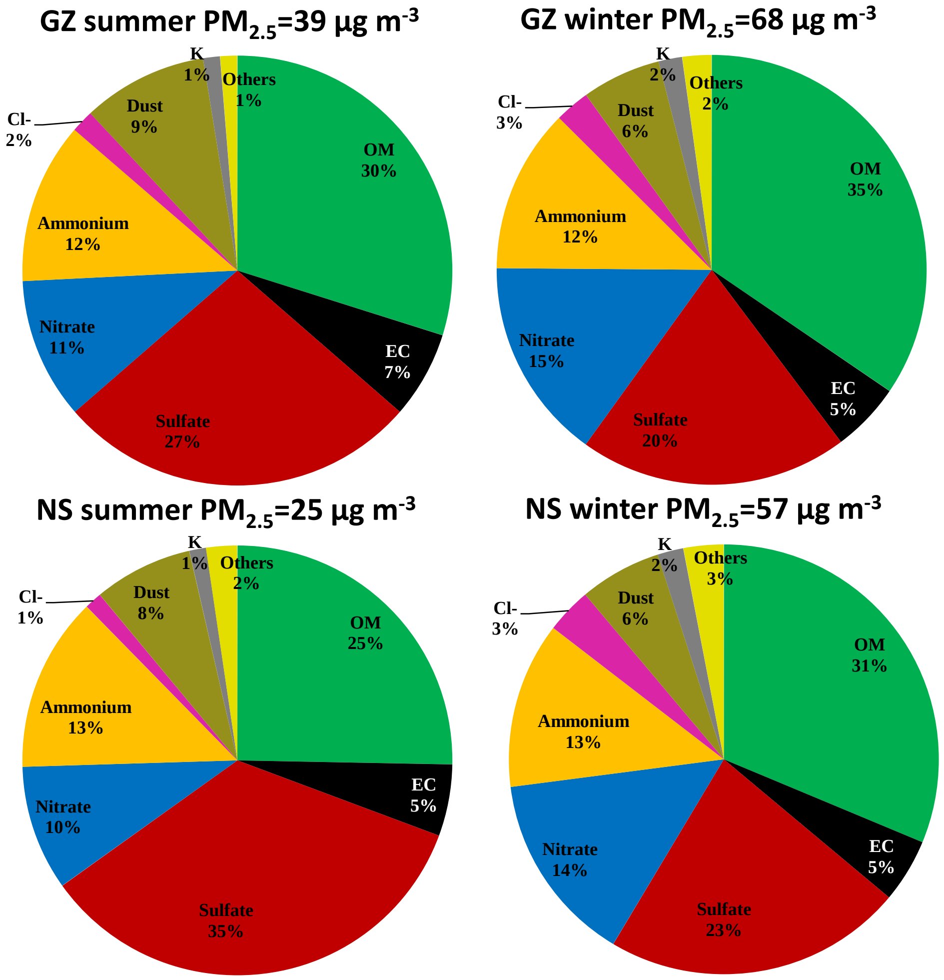

Fig. R1 Average concentration and composition of $PM_{2.5}$ in GZ and NS in summer and winter. Organic Matter (OM)=1.4xOC. Dust= 2.2[Al] + 2.49[Si] + 1.63[Ca] +2.42[Fe] + 1.94[Ti] (Huang et al 2014)

7. Further explanation is needed on page 23920, line 23-24 – how was the WSOC proportion consistent with their suburban and urban location characteristics?

Response: The following text is added to provide a brief explanation:

> Lines 216-220:
> "NS as a suburban site is a receptor site for urban pollution. Aerosols arriving at NS have undergone a certain degree of atmospheric processing, thus OC in the aerosols would be more oxidized and more of the OC fraction would become water-soluble. As such, WSOC/OC would be expected to be higher at NS than the urban site GZ."

8. At line 23920, line 21 – a surprisingly large fraction of the OC was water soluble at 96%. Are these results consistent with measurements of PAH and alkanes? What conditions gave rise to such high WSOC levels? Related, and because the goal is to show that WSOC was a significant fraction of OC, perhaps the averages are a better statistic to use than the maxima.

Response: We agree that the averages are a better statistic than the maxima values in illustrating the significant presence of WSOC in OC. We now have deleted the half-sentence “accounting for as high as 61% of OC at GZ and 96% at NS”.

Regarding the high WSOC/OC ratio (96%) on 26 May in NS, more information is given below. On this day, $PM_{2.5}$ was low at the level of 23.6 μg/m^3, OC was 5.00 μgC/m^3, and WSOC was 4.78 μgC/m^3. The back trajectory analysis indicates that marine air mass influenced the site on that day, likely bringing in more aged aerosols (therefore more oxidized OC and higher WSOC/OC). The levels of PAHs and alkanes were low, consistent with the WSOC/OC data.

9. Page 23921, lines 1-3 – While the absolute concentrations of WSOC were higher in autumn and winter, but the relative contributions to OC were lower. Why? The absolute levels are likely affected by seasonal patterns and meteorology, which will affect PM mass loadings and other components. Discussion of the relative levels of WSOC across seasons reflects different sources, and ties in with the other objectives of this manuscript.

Response: The following is the discussion of seasonal variation of WSOC and OC.
Table R1 shows the seasonal average of WSOC, WISOC, OC, PM2.5 and WSOC/OC ratio. The two components of OC, WSOC and WISOC, do not share the same emission sources/formation processes or removal rate. As such, WSOC and WSOC/OC do not necessarily share the same seasonal variation trend. If we compare summer and winter for GZ samples, WSOC in winter was 1.67 times WSOC in summer but the increase in WISOC in winter was more than WSOC. As a result, WSOC/OC decreased in winter in comparison with in summer at GZ. At NS, WSOC was lower in the summer than in winter but WSOC/OC was higher in the summer. WSOC is generally low in summer, likely a result of faster wet removal due to frequent rain events in this season.

Table R1. Seasonal average of WSOC, WISOC, OC, PM2.5 and WSOC/OC ratio

	WSOC μgC/m^3	WISOC μgC/m^3	OC μgC/m^3	WSOC/OC %	$PM_{2.5}$ μg/m^3
GZ-spring	4.34	8.01	12.35	35.7	73
GZ-summer	**3.56**	**4.77**	**8.33**	42.5	**39**
GZ-autumn	5.95	6.67	12.62	48.5	55
GZ-winter	6.01	10.81	16.82	36.7	68
NS-spring	3.95	7.63	11.57	35.8	62
NS-summer	**2.52**	**2.02**	**4.55**	57.0	**25**
NS-autumn	5.32	5.87	11.20	46.0	51
NS-winter	4.96	7.85	12.81	41.0	57

10. Page 23921, lines 13-15: I am confused by “HULIS and WSOC may differ in their major contributing sources.” Isn’t HULIS a part of WSOC, so they have to have in part some of the same sources? Or maybe this says there are different sources of WSOC_h? Or maybe the sentence is not clear and should this be qualified to say: “The difference in absolute concentrations of HULIS and WSOC across the two study sites suggests that each site is impacted to different extents by WSOC sources.” ?

Response: WSOC consists of HULIS and WSOC_h. The two fractions of WSOC_h could have different sources.
This sentence is rephrased to be (Lines 235-236):
"HULIS and the rest of WSOC may differ in their major contributing sources."

11. Page 23921, lines 15-22 does an excellent job of comparing results of this study to prior studies. It is this level of discussion that is encouraged to be expected to PM2.5 and other key components in this manuscript.

Response: We wish to clarify that the comparison of $PM_{2.5}$ and key components with other studies is not the focus of this study, and addition of this content will dilute this focus.

12. Page 23921 line 27: The correlation between HULIS and levoglucosan does not "indicate that biomass burning was a source of HULIS in the winter", rather it indicates that they covary in time and suggests that they may be derived from the same source.

Response: In a previous study, we collected biomass burning source samples (rice straw burning and sugar cane leaves burning samples) and quantified HULIS from these source samples (Lin et al 2010). It is found that BB emissions from crop residue burning produce HULIS.

13. The paragraph beginning on page 23921, line 23 should be combined with the discussion of Figure 4 and section 3.2.1.

Response: Suggestion taken. The last paragraph of 3.1.2 is moved to and combined with section 3.2.1.

14. Because of the seasonal differences, correlations between sulfate and levoglucosan with HULIS may be more demonstrative if broken into "summer" and "winter" in Figure 4.

Response: Thanks for the suggestions. The following plot (Figure R2) was added to the supplementary materials (Figure S6). The figure shows that correlation of HULIS vs levoglucosan is much better in winter than in summer, which is consistent with PMF result that biomass burning source is more important in winter than summer. The correlation of HULIS vs sulfate is similar in winter and in summer, which agrees with the PMF results that secondary process is important in the whole year.

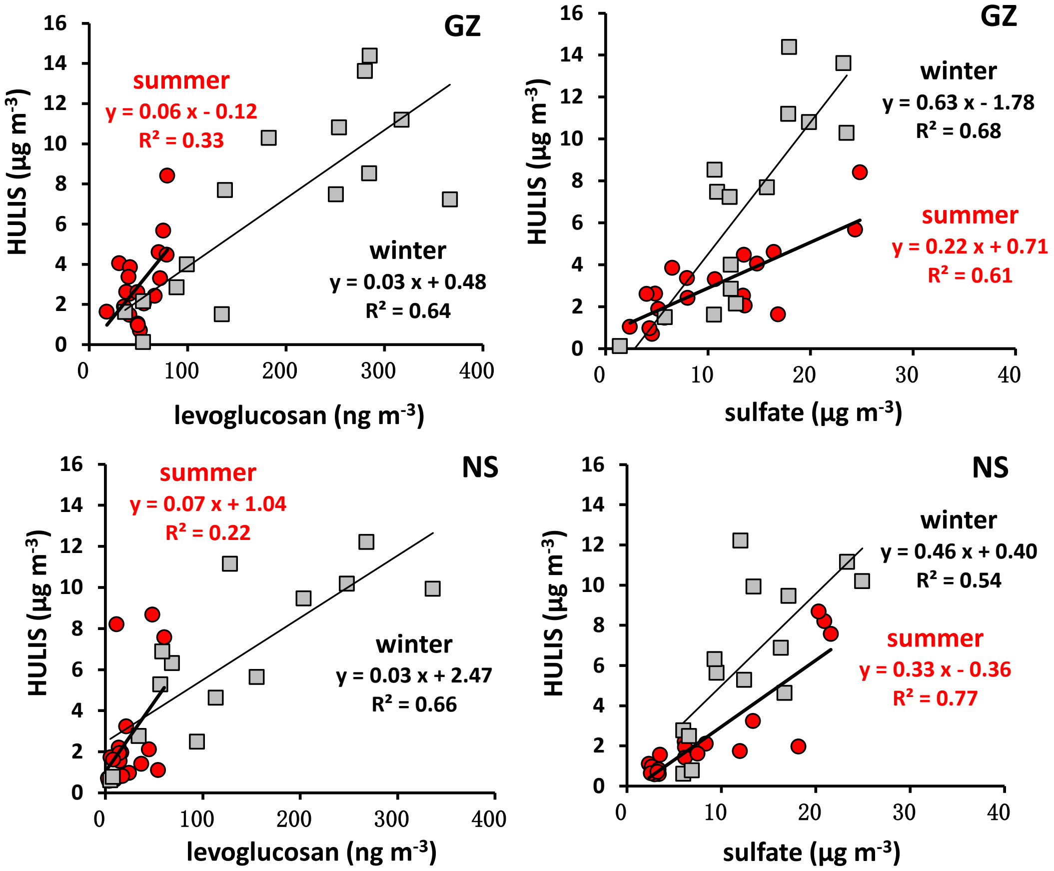

Fig. R2 Correlations of HULIS with levoglucosan and sulfate in summer and winter

15. Is there evidence that the two sites are impacted by different types of biomass burning? This could be assessed by comparison of levoglucosan/mannosan, levoglucosan/ galactosan ratios or levoglucosan/K ratios across the two sites. Since different types of biomass (i.e. agricultural burning or wood burning) can produce emissions of different chemical composition, this should be ruled out as a potential source of the spatial differences in levoglucosan concentrations discussed on page 23922 line 6. Moreover, these ratios (mentioned at line 23923, line 9-11) can be used to gain insight to the types of biomass impacting the site during the various seasons.

Response: Thanks for the suggestions. It seems that the two sites are impacted by similar types of biomass burning on the basis of levoglucosan/mannonsanm and levoglucosan/galactosan ratios. In Figure S1, levoglucosan vs mannosan, and levoglucosan vs galactosan of all the data in both sites show good correlation (R^2=0.94 and 0.82 respectively). The levoglucosan/ mannosan ratio was in the range of 5~17 (most data are in 7~10) all the year. The levoglucosan/ mannosan of shrub burning was 9.8±2.1 (N=12) in a study reported by Munchak et al (2011), which is between the ratio of softwood burning (3~5) and hardwood burning (14~15) (Engling et al 2009). Thus, both sites may be affected by shrub burning, but we cannot exclude the possibility that both sites are affected by a mix of other kinds of biomass burning.

References:

Engling, G., Lee, J. J., Tsai, Y. W., Lung, S.C.C., Chou, C.C.K., Chan, C.Y.: Size-Resolved Anhydrosugar

Composition in Smoke Aerosol from Controlled Field Burning of Rice Straw, Aerosol Science and Technology, 43, 662-672, 2009.
Munchak, L.A., Schichtel, B.A., Sullivan, A.P., Holden, A.S., Kreidenweis, S.M., Malm, W.C., Collett, J.L.: Development of wildland fire particulate smoke marker to organic carbon emission ratios for the conterminous United States, Atmospheric Environment, 45, 395-403, 2011.

16. Are the two sites impacted to different extents by agricultural burning? This is an important consideration because of its contribution to HULIS.

Response: Since it seems that the two sites are impacted by similar types of biomass burning (in Response to comment 15), the reason of higher levoglucosan in GZ than in NS could be: (1) the two sites were impacted by biomass burning to different extents (more intense in GZ than in NS); (2) GZ site is nearer to biomass burning sources than NS site is.

17. Ensure the reference to HYSPLIT is properly cited.

Response: Suggestion taken. The proper citation is added to the references.

18. Page 23923, line 22: Provide a numerical statement of the “low correlation” coefficient observed for vehicle, dust, and ship emission tracers.

Response: Suggestion taken. The R^2 values are provided in the 3.2.1 paragraph.

19. Table 1 contains substantial valuable information, but is rather difficult to follow. The following suggestions are intended to improve the readability and utility of the table: a. The authors should consider significant figures in making this table. The standard deviation should have 2 digits and the mean should be adjusted to match. For example, 12.39 _ 6.79 for sulfate, should be 12.4 _ 6.8. b. The mean _ standard deviation should be in one column and the range in another. Together, the numbers are too close and difficult to follow. c. “C2O4=” should be “oxalate” to match the text. d. It is suggested to break the table into addition sub-sections, “PM2.5 and carbon fractions” “Ions” “Trace elements” and “Organic Tracers” Appropriate units can be given in the sub-title. e. Ti, Ni should not have a minimum value or standard deviation of 0

Response: Thanks for these suggestions. Table 1 is modified accordingly.

20. Figure 1 – Can a brighter circle be used to mark the study sites instead of pin? It is difficult to see, especially in black and white. The red text is also difficult to see.

Response: Suggestion taken. The labels of the study sites are changed accordingly in Figure 1.

21. Ensure that consistent units for levoglucosan are used throughout the text and figures – Figure 3 and 4 show ng and ug per cubic metre.

Response: Suggestion taken. Because levoglucosan is always <1 ug per cubic meter, it is proper to express levoglucosan using ng per cubic meter. The unit of levoglucosan in Figure 4 is changed to ng per cubic meter.

22. Figure 4 – January 26 can be removed from this figure and caption, since its differences due to New Year is noted.
Response: Suggestion taken. The January 26 data point is removed from Figure 4.

23. The x-axis in Figure 5 should be reordered to follow table 1. In addition, the chemical names should match what is in the text (i.e. oxalate, OC, EC).
Response: Suggestion taken. Figure 5 is modified accordingly.

24. Page 23920 – line 3: “summary statistics”
25. Page 23928 – line 1: “residual oil”
Response: Corrected.

26. Page 23929 – line 8-10 should be omitted, as it has not been peer reviewed.
Response: We are not clear which reference the reviewer refers to. The reference Miyazaki et al (2009) cited here is published in J. Geophys. Res.- Atmos

27. Page 23930 – For consistency, use NS and GZ abbreviations in conclusion.
Response: Corrected.

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 _g C m-3 (or HULISC). 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 $PM_{2.5}$ ambient samples in PRD region was determined to be 1.94±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_h data from WSOC and HULIS_C and subsequently the investigation of WSOC_h sources. The following text is added to the revised paper to explain the use of HULIS-C:

> Lines 137-139:
> “Using HULIS-C allows the easy derivation of WSOC_h data from WSOC and HULIS_C and subsequently the investigation of WSOC_h 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.

> Lines 352-364:
> “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, α-pinene, β-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 (SO42- and NH4+) (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 (Lines 112-114):

> "For the analysis of WSOC and HULIS, portions of the quartz filters were extracted by

> sonication in ultrapure water (>18MΩ•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 (Lines 122-129):
"Briefly, the aerosol water extract was acidified with HCl to pH≈2, then loaded to the SPE cartridge (Oasis HLB, 30 μm, 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 (Lines 160-162)

> "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.

Anonymous Referee #3

Overview: This paper reports the composition of aerosol collected every 6 days at two sites in the Pearl River Delta. The sites, Guangzhou and Nansha, represent urban and suburban sites in southeastern China near Hong Kong. Although several PM2.5 components were measured, HULIS is the main focus in this paper. HULIS is defined as the SPE extractable compounds of water-soluble organic carbon (WSOC). Thus, it excludes the highly water-soluble organic anions that can represent a large fraction of the total WSOC. However, the composition of the SPE extractable compounds is expected to vary widely, thus it is not a specific sub-fraction of WSOC. For example, terpene SOA, isoprene SOA, biomass burning OA (BBOA), aged OA components and other slightly oxidized components are likely to contain high molecular weight species that can be retained using reversed phase SPE. This fairly non-specific fraction of WSOC represented 48 and 57% of the measured WSOC at the two sites. In this work, the authors use positive matrix factorization of the measured components (N = 27) to determine the emission sources of HULIS. They reported a major fraction (49 – 82%) to be from secondary processes (SOA and aged OA are implied), biomass burning, residual oil combustion and marine emissions were also identified. The authors were surprised by the finding of residual oil combustion associated with ship traffic from the nearby seaports. Given the transient nature of OA compounds in the atmosphere and the non-specific class of compounds likely retained by the SPE, the result is reasonable. Shipping between continents appears to be a large source of pollution that is especially understudied. The significance of this result is somewhat buried in the details for the source apportionment and yearlong study of composition. Although some attention to the back trajectory analysis was done, it would have been very nice to see the samples grouped by source regions instead of month. Perhaps this is difficult to do, because the wind direction may change over the course of the sampling period. However, consideration to the meteorology could really help in the interpretation of the observations.

Response: Thank the reviewer's overview comments on the paper.

(1) We echo the point that HULIS is a fraction of WSOC defined by the analytical procedure for its isolation, thus consists of possibly a wide range of compound classes (classified by functional groups). The isolation procedure of HULIS determines that its constituents are hydrophobic, excluding the highly water-soluble organic compounds (often of relatively low molecular weights). These hydrophobic WSOC species are often not readily amenable to solvent extraction-GCMS analysis, consequently largely ignored in earlier organic aerosol speciation work. The exploration of the sources for HULIS, this non-specific group of OC, will shed insights in improving characterization of the more source-specific and the more compound class-specific aerosol organics.

(2) We agree with the review that ship emission is a significant, but understudied, source of PM pollution cities near seaports. In this work, we have relied on both chemical information and back trajectory analysis in affirming the influence of ship emissions. Variations of HULIS source contributions by month and by air mass origins are presented, in Table 2 and Figure 7, respectively.

Specific comments:

1. The introduction of the manuscript is quite succinct and does not appear to include recent

references on the composition of HULIS. Considerable study of HULIS in this region has been previously presented by these authors, but is hardly summarized here. Plus, quite a bit of complementary study has been done by other groups. Some review of this material would be useful to readers and would help to define what is known about HULIS.

Response: A brief summary of recent literature about composition of HULIS are added to the introduction part.

> Lines 63-67:
>
> "The molecular composition of HULIS was also studied using ultrahigh resolution mass spectrometer (e.g. Wozniak et al., 2008; Lin et al., 2012a; 2012b; Yassine et al., 2012). Through composition study, it was confirmed that biomass burning and secondary formation process were sources of HULIS (Lin et al., 2012a)."

2. PMF discussion is fragmented. a. There are method details in the Results and discussion section. Those details should be moved to the Experimental section. b. Background of PMF source apportionment is given in the Experimental section, since PMF is used to discern HULIS sources it seems appropriate to include the relevant PMF literature review in the introduction.

Response: (a) In the Result and discussion section 3.2.2, two methods were described in determining the number of factors in PMF, followed by showing the determination of factors. Thus we think it is more appropriate to leave this part in this section.

(b) Suggestion taken. We have moved the brief review of PMF literature to the Introduction section.

3. Where did the conversion of measured HULIS mass to HUIS-C come from?

Response: 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 $PM_{2.5}$ ambient samples in PRD region was determined to be 1.94±0.11. We have cited the work by Kiss et al (2002) and Lin et al (2010) in the text to indicate the source of this conversion factor.

4. Evaporative light scattering is universal detector for LC, but it has some serious limitations with respect to the dynamic range. How were these limitations avoided?

Response: The dynamic range of ELSD is up to 250 mg/L. If we detected a sample with its concentration exceeding 250 mg/L, we diluted the extracted sample solution to an appropriate concentration and measure again. The following text is added to include information on the ELSD dynamic range.

> Lines 129-131:

> “Routine calibration of ELSD was carried out using standard solutions of SRFA (Suwannee River Fulvic Acid, International Humic Substances Society) up to 250 mg/L (the upper limit of the ELSD dynamic range).”

5. Several studies are showing compelling evidence of reactions between ammonia and carbonyl containing compounds (e.g., Yu et al., 2011 show that glyoxyl and NH3 react to form imidazole). Since these reaction products are likely to be hydrophobic, how are these potential artifacts avoided in the SPE method?

Response: Yu G. et al (2011) found that the reaction of glyoxal with ammonium sulfate is quite slow. When 1M glyoxal was mixed with 1M ammonium sulfate solution, 4% of initial glyoxal reacted in a week. On the basis of this observation, they suggested that this reaction unlikely contributes significantly to ambient secondary organic aerosol. In our SPE extraction, the HULIS fraction was eluted from the SPE cartridge with 1.5 mL methanol containing 2% (w/w) NH_3, then the solution is blown to dry under gentle nitrogen gas. The whole procedure takes less than 2 hours. Hence, the artifacts resulting from NH_3 reactions with carbonyls are unlikely significant.

Reference:

Yu, G., Bayer, A. R., Galloway, M. M., Korshavn, K. J., Fry, C. G. and Keutsch, F. N.: Glyoxal in Aqueous Ammonium Sulfate Solutions: Products, Kinetics and Hydration Effects, Environmental Science & Technology, 45, 6336-6342, 2011.

6. It is stated that “Obvious seasonal variation of WSOC was observed: : :”, but some of the days in December have lower mass concentrations than July. The patterns shown here may have seasonality effects, but they also have other meteorological effects that obscure the seasonal variation.

Response: As seen in Figure 2 shows that, OC and also WSOC were very low on 2 days in winter, namely November 16 and December 16. We checked the meteorological conditions on these two days. It was raining and cloudy on these 2 sampling days. The raining events likely effectively removed PM and led to low PM2.5 (and constituents) on the two days: 8.5 μg m^{-3} on 16 Nov in GZ; 21 μg m^{-3} on 16 Dec in GZ; 26 μg m^{-3} on 16 Dec in NS. On average the winter WSOC was higher than the summer. The following sentence is added to explain the two low PM mass concentration days.

> Lines 224-225:
> “Two winter days (16 November and 16 December) were exceptional, with lower concentrations of $PM_{2.5}$, OC and WSOC as a result of rain events.”

7. What is the meaning of the WSOC/OC% in figure 2?

Response: WSOC/OC% means the percent WSOC in OC. Fig. 2 caption is revised to include the following text to explain WSOC/OC%:

> “Data of the percent of WSOC in OC are shown as line curves.”

8. The concentrations of HULIS are described as being nearly identical between the two sites, however the axes are different and thus it's not clear in figure.

Response: We state in the paper that the annual average concentrations of HULIS (shown in Table 1) were similar at the two sites. We wonder whether the referee is referring to Figure 2, in which we have different y-axis scales so that the visual viewing of individual subfractions of OC could be optimized. Comparing HULIS concentrations at the two sites for the same time windows can be seen through Figure 3, which has the same scale for HULIS.

9. Why do you observe a correlation between sulfate and HULIS, does this indicate aqueous SOA processes?

Response: The positive correlation between sulfate and HULIS is likely a broad indication that a significant fraction of HULIS is formed through the same secondary processes such as in-cloud processing as sulfate and/or heterogeneous reactions involving sulfate aerosols. Below text is added to elaborate on the secondary formation as a HULIS source.

> Lines 352-364:
> "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, α-pinene, β-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."

10. Little to no discussion of why "outliers" were removed from the statistical analysis of correlations was provided. Other than the position in the plot, are there other reasons to suspect measurement errors? What about the non-zero y-intercept?

Response:
(1) The outliers in Figure 4 are on January 26, 2009, which coincided with Chinese New Year. We suspect festival-related activities (e.g., fireworks) affected the $PM_{2.5}$, as stated in the manuscript. Levoglucosan, a biomass burning tracer, was extremely high on that day. The high levoglucosan concentration is not likely due to measurement errors, as repeat analysis of filter punches from the same filter confirmed the high concentration. We excluded the data from PMF analyses in order not to distort the result of source apportionment.

(2) The non-zero y-intercept of HULIS vs levoglucosan in Figure 4 indicates that besides biomass burning, there are other sources (e.g., secondary formation) contributing to HULIS.

11. Figure 4 has inconsistent fonts in the x-axis labels.

Response: Suggestion taken. The fonts in the x-axis are changed to the same.

12. The data in Table 1 is given in at least 3 different ranges of mass concentrations; perhaps some reorganization can clarify the data presentation. Also, too much data is given. What is the purpose of giving the range of concentrations? Perhaps box plots could be used to indicate the distribution of the measurements.

Response: Table 1 is revised per suggestion from Referee #1 so that it is easier to comprehend the summary statistics of key major components and traces used in the source apportionment. The table serves a similar purpose to using a boxplot. Listing the measurements in numbers has the advantage of providing readers with exact numerical values.

13. Figure 3 does not clearly indicate correlations. What about error bars for these measurements?

Response: Figure 3 shows the time series of HULIS, levoglucosan and sulfate. We intend to use this figure to indicate the rough correlation (simultaneous up and down of the concentrations) by visual inspection and similarity/difference in temporal variation patterns of the three species. The trends of levoglucosan and HULIS were similar in winter, but not in summer. HULIS tracked sulfate well in summer as well as in winter. A more quantitative assessment of correlation is shown by Figure 4. The error of HULIS, levoglucosan, and sulfate are estimated to be 10% of their concentration.

14. On page 23923, the authors indicate R2 _ 0.4 is slightly positive. This seems quite generous. What is the basis for this? Were outliers removed or retained?

Response: The two samples on January 26 were removed. Through positive correlation is statistically significant at 95% confidence level.

15. Correlations between aerosol mass and vanadium were previously observed, but no references were provided. The correlation between HULIS-C and V as shown in figure 8 appears to be very strongly influenced by an "outlier". What is the R2 if the point is removed?

16. Likewise, the correlation between HULIS-C and Na+ is strongly influenced by an outlier. What does this look like if the point is removed? Also, is it possible those outlier points are the same outliers ignored in the previous correlation analysis?

Response to comments 15 and 16:
(1) Two references (Kowalczyk et al., 1982; Chow and Watson, 2002) are added to support V as a tracer for residue oil combustion emissions (Line 403).

(2) The points in Figure 8 are all in summer, while the outliers in Figure 4 are on Jan 26. They are different samples.

(3) For Figure 8, if the high-HULIS-concentration point is removed, the R^2 of HULIS vs V becomes 0.33, while the R^2 of HULIS vs Na^+ becomes 0.01. They are both lower than the R^2 shown in the manuscript. The correlation of HULIS vs V is not that strong, as it is difficult to fully tease out the contributions from other HULIS sources (e.g., secondary formation, biomass burning) and also because the limited number of data points falling in the category of “marine days in NS site”. Results from this study provide preliminary evidence for the suggestion of ship emissions as a HULIS source. Further studies are needed to collect more ambient samples affected by ship emissions.

References

Chow, J.C. and Watson, J.G. (2002). Review of PM2.5 and PM10 Apportionment of Fossil Fuel Combustion and Other Sources by Chemical Mass Balance Receptor Model. Energy Fuels 16: 222–260.

Kowalczyk, G.S., Gordon, G.E. and Rheingrover, S.W. (1982). Identification of Atmospheric Particulate Sources in Washington D.C. Using Chemical Element Balances. Environ. Sci. Technol. 16: 79–90.

17. The correlations shown in figure 8 plots for HULIS-C vs. V and Na+ are not strong enough to “: : :clearly implicates shipping emissions: : :” Further study of those correlations is needed to justify ship emissions as a source of HULIS as stated in the conclusions and abstract.

Response: Suggestion taken. We revised this statement as the following:

> Line 407-412:
> “The positive correlation between HULIS-C and V and lack of correlation between HULIS-C and Na^+ in the subset of the NS samples (n = 16) implicates shipping emissions, not sea salt, as a source of HULIS. Since the number of data points collected on the “marine” days in NS site is small, further studies are needed to collect more ambient samples affected by ship emissions to confirm the link between residual oil combustion emissions and HULIS.”