Response to Review Comments (acpd -14-23913-2014)
Response to comments by 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.

> "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.

> "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.

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.

> "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.

> "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 etal., 1982; Chow and Watson, 2002) are added to support V as a tracer for residue oil combustion emissions.

(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:

> “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.”