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# ***Interactive comment on “Sources of humic-like substances in the Pearl River Delta, China: positive matrix factorization analysis of PM<sub>2.5</sub> major components and source markers” by B. Y. Kuang et al.***

**Anonymous Referee #3**

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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 PM<sub>2.5</sub> 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

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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.

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. 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. 3. Where did

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the conversion of measured HULIS mass to HUIS-C come from? 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? 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 NH<sub>3</sub> react to form imidazole). Since these reaction products are likely to be hydrophobic, how are these potential artifacts avoided in the SPE method? 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. 7. What is the meaning of the WSOC/OC% in figure 2? 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. 9. Why do you observe a correlation between sulfate and HULIS, does this indicate aqueous SOA processes? 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? 11. Figure 4 has inconsistent fonts in the x-axis labels. 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. 13. Figure 3 does not clearly indicate correlations. What about error bars for these measurements? 14. On page 23923, the authors indicate  $R^2 \geq 0.4$  is slightly positive. This seems quite generous. What is the basis for this? Were outliers removed or retained? 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 R<sup>2</sup> if the point is removed? 16. Likewise, the correlation between HULIS-C and Na<sup>+</sup> is strongly influenced by an outlier. What does this look like if the point is removed? Also, is it

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possible those outlier points are the same outliers ignored in the previous correlation analysis? 17. The correlations shown in figure 8 plots for HULIS-C vs. V and Na<sup>+</sup> 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.

References Yu, G., A. R. Bayer, M. M. Galloway, K. J. Korshavn, C. G. Fry and F. N. Keutsch (2011). "Glyoxal in Aqueous Ammonium Sulfate Solutions: Products, Kinetics and Hydration Effects." *Environmental Science & Technology* 45(15): 6336-6342.

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