

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:

“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 PM_{2.5} component was set as the master variable in PMF modeling. I could reasonably assume PM_{2.5} 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:

“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 µg/m³) than NS (44 µg/m³) during this study period. They were lower than measurements obtained for the period of July 2007-August 2008 (GZ: 78 µg/m³, NS: 66 µg/m³) (Lin et al., 2010b). Seasonally, PM_{2.5} was higher in winter (GZ: 68µg/m³, NS: 57µg/m³) than summer (GZ: 39µg/m³, NS: 25µg/m³) (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.”

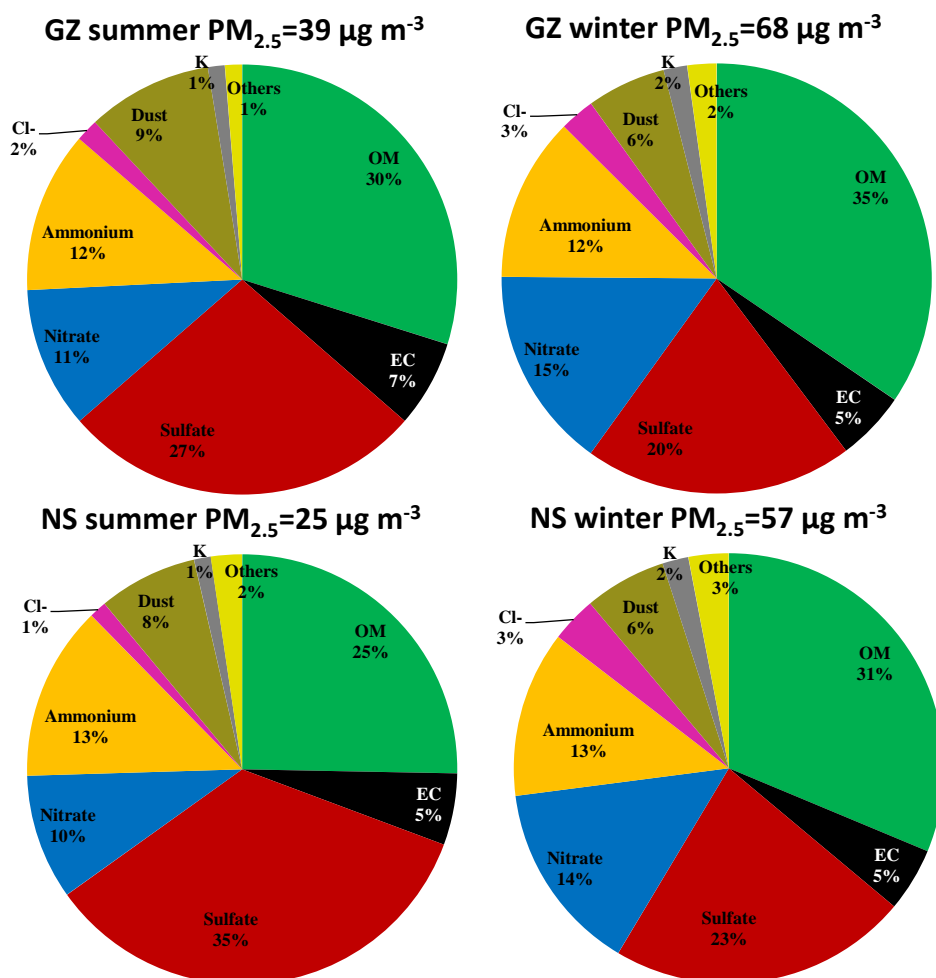


Fig. R1 Average concentration and composition of PM_{2.5} in GZ and NS in summer and winter. Organic Matter (OM)=1.4xOC. Dust= 2.2[Al] + 2.49[Si] + 1.63[Ca] +2.42[Fe] + 1.94[Ti] (Huang et al 2014)

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:

“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/m³, OC was 5.00 µgC/m³, and WSOC was 4.78 µgC/m³. 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, PM_{2.5} 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. At NS,

Table R1. Seasonal average of WSOC, WISOC, OC, PM_{2.5} 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:

“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 PM_{2.5} 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 into 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.

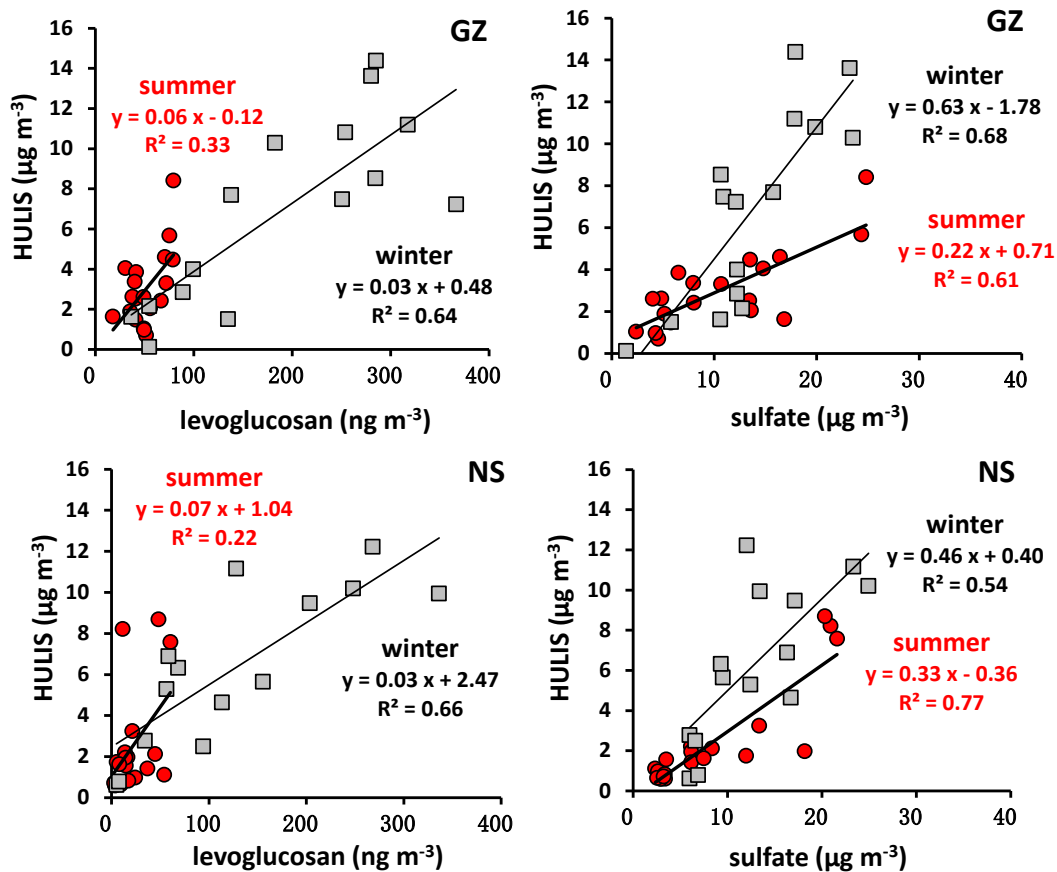


Fig. R2 Correlations of HULIS with levoglucosan and sulfate in summer and winter

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/mannosan 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.

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.

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.

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

Thanks for these suggestions. The 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.

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.

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

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).

Thanks for these suggestions. Figure 5 is modified accordingly.

24. Page 23920 – line 3: “summary statistics”

Corrected.

25. Page 23928 – line 1: “residual oil”

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.

Corrected.