

Anonymous Referee #2

This work integrates ambient, source sample measurements and modeling investigation to quantify HULIS sources in Beijing. This integrative approach provides quantitative insights into HULIS sources that otherwise are not easily extracted from source and ambient measurements alone. The paper is well-written and easy to follow. I have one main concern regarding the estimation of secondary HULIS. It is estimated to be the difference of measured HULIS and modelled primary HULIS. The difference method is inherently associated with large uncertainty and it appears less reliable (see more details in the specific comments). Any overestimate in primary HULIS would translate to underestimate in secondary HULIS. It is desirable that the authors conduct a receptor model source apportionment (such as positive matrix factorization) using the measured chemical composition to estimate the secondary HULIS contribution and inter-compare with the results obtained from the CMAQ model.

Response: We thank the reviewer #2 for instructive comments to help us improve the manuscript. We have conducted a receptor model source apportionment (PMF) to estimate source contribution to ambient HULIS (including the secondary HULIS contribution) and inter-compared with the results obtained from the CMAQ model. The work has been submitted to “Science of Total Environment” for reviewing.

Below are our responses to reviewer comments including descriptions how we have modified the manuscript.

Specific comments:

1. Model evaluation of HULIS. Fig. 4 compares predicted primary HULISc and observed HULISc on days with relative good primary PM_{2.5} model performance. In the main text it is reported fractional error of less than 0.6 was used to select the good model performance data. What is the percentage of data in this work's dataset fall outside this criterion of good modeling performance? Are there any patterns in the sub-group of data with poor agreement?

Response: The percentage of data fall outside the “good” performance range in spring, summer, autumn and winter is approximately 12% (3/25), 30% (8/26), 55% (18/33) and 25% (7/27), respectively. We noticed that on these “bad” performance days, the model significantly overpredicted concentrations of PPM_{2.5} in autumn and winter, with a mean fractional bias (MFB) of 1.16 and 0.64, respectively. For spring and summer, the model under-predicted PPM_{2.5} with MFB of -0.39 and -0.21, respectively, on the bad performance days. In comparison, for good model performance days, the MFB values are -0.09 (spring), 0.15 (summer), -0.05 (autumn), and -0.08 (winter). The average concentrations of estimated PPM_{2.5} during these bad performance days are 76 $\mu\text{g m}^{-3}$ (spring), 68 $\mu\text{g m}^{-3}$ (summer), 9 $\mu\text{g m}^{-3}$ (autumn) and 32 $\mu\text{g m}^{-3}$ (winter). In contrast, the averaged PPM_{2.5} on the good performance days are 46 $\mu\text{g m}^{-3}$ (spring), 33 $\mu\text{g m}^{-3}$ (summer), 34 $\mu\text{g m}^{-3}$ (autumn) and 103 $\mu\text{g m}^{-3}$ (winter). From this analysis, it is evident that the observed PPM_{2.5} concentrations on the bad model performance days are quite different from that on the good performance days. The CMAQ model performance decreases when the observed concentrations are higher or lower than the normal concentration for that season. It is probably because that the day-to-day variations in the emission are poorly represented in the emission processing (currently, only weekday-weekend differences are considered in each month). The good day results reported in this study are representative of common conditions within each season.

2. In this work, contributions of HULISc from secondary processes were determined by subtracting predicted primary HULISc from observed HULISc. The percentage contribution of secondary process was 40.2% in summer, 52.7% in fall, 14.3% in winter and 13.1% in spring. The secondary HULIS contribution was surprisingly low, considering the strong correlations of

HULIS with secondary PM components such as sulfate and estimated SOC, especially for winter samples (Figure 3).

Response: According your Comment 4, we double checked foc and HULISc/OC data sources and revised the data (see detail in Comment 4 Response). The revised calculation leads to more secondary HULISc. The percentage contribution of secondary process is 50.2% in summer, 63.2% in fall, 30.3% in winter and 25.4% in spring, with annual average contribution of 38.9%.

3. Related to the previous comment, and also the fact that on some days the predicted primary HULISc concentrations are greater than the observed HULISc, I have the concern whether certain assumptions made in the model have led to positive bias for primary HULISc (therefore negative bias for secondary HULISc) (e.g., assumption of foc values, see the next comment). How many samples were predicted by the model to have negative secondary HULISc? Are there any common characteristics in these samples that might shed some insights for the potential bias?

Response: Thirty-two (32) days out of 72 have negative secondary HULISc. However, the negative values are usually very low (-1.40 ± 1.49 , one standard deviation). These days are usually associated with low total HULISc concentrations (2.73 ± 3.10). Thus, this treatment does not introduce significant bias in the estimation of secondary HULISc overall.

4. Table S3 lists the values of foc for primary sources considered in the model. “Residential” source has the largest foc at 62.80%. It appears this residential source is residential coal combustion (#91028) (Ying et al, 2018). Was this Residential source foc also applied to residential biofuel burning? If yes, is there supporting evidence for this assumption? The apportionment of primary HULIS sources by the CMAQ model in this work suggested that residential biofuel burning was the largest HULIS source year around (34-70%), and especially dominant during winter and spring (70%). The foc in open biomass burning (arguably a burning activity bearing similarity to residential biofuel burning) is 29.40%, only $\frac{1}{2}$ of the foc for residential coal combustion. Apparently, the foc value assumed has a large impact on the modeled source contribution. The authors need to clarify what foc value is adopted for residential biofuel combustion and the rationales behind.

Response: Thanks for the suggestion. #91028 is for residential coal combustion. We have adopted foc for residential biofuel burning at 42.51% based on field measurement in China (Li et al., 2009).

Li X., Wang S., Duan L., Hao J., Nie Y. Carbonaceous aerosol emissions from household biofuel combustion in China. Environmental Science & Technology, 2009, 43: 6076-6081.

We double checked foc data source of open burning and found that #92084 is not for biomass open burning, thus we removed it and averaged #92000 and #92090 and obtained the foc for open biomass burning at 42.29%.

We adopted HULIS_c/OC for open burning same as biofuel combustion (44%, from our measurement) previously. However, when we compared HULIS_c/OC from open burning and biofuel combustion, we found difference between them. For biomass open burning, HULIS-to-OC ratios varied less (from 0.14-0.35), while for biomass burned in the stove, ratios varied a lot (from 0.01-0.50). For advanced stove used in European (with secondary air), combustion is relatively complete, thus HULIS produce less (0.01-0.12), while for stove used in Chinese rural household, combustion is relatively inadequate, thus HULIS produce more (0.41-0.50). We think combustion condition has much influence on the HULIS-to-OC ratios. For stove used in European and China, biofuel is burned in a relatively enclosed combustion chamber. Dilution ratio (DR) and residence time (RT) could affect gas-particle partitioning, and thus also have effect on the results (Lipsky et al., 2006; May et al., 2013). Thus we adopted HULIS_c/OC for open burning at 25% (average value of previous references about biomass open burning).

Biomass	Combustion condition	Sampling condition	HULIS _c /OC	HULIS _c /WSOC	Reference
Wood (M=9.3%)	Improve stove	Chamber/hood DR≈40, RT≈80s	0.41±0.07	0.62±0.06	This study
Wheat straw (M=9.8%)	Improve stove	Chamber/hood DR≈40, RT≈80s	0.50±0.04	0.65±0.05	This study
Maize stover (M=8.0%)	Improve stove	Chamber/hood DR≈40, RT≈80s	0.42±0.04	0.62±0.04	This study
Wood	Chimney type	Dilution source sampler with DR=10, RT long enough (no	0.04-0.11		Goncalves et al., 2010

(M=7~14.8%)	logwood stove with primary/secondary air	specified)			
Wood (M=10~16%)	Domestic tile stove	Dilution sampler with DR=3, RT=0.2s	0.01-0.12		Schmidl et al., 2008a
Leaves (M=25%)	Open burning	Smoke plume	0.33-0.35		Schmidl et al., 2008b
Rice straw (M=5.8%)	Open burning	Chamber		0.66±0.02	Fan et al., 2016
Corn straw (M=7.4%)	Open burning	Chamber		0.59±0.02	Fan et al., 2016
Pine branch (M=7.6%)	Open burning	Chamber		0.57±0.03	Fan et al., 2016
Rice straw	Open burning and chamber	Chamber/hood or downwind	0.34±0.05		Lin et al., 2010a
Sugarcane leaves	Open burning	Chamber/hood	0.28±0.03		Lin et al., 2010a
Charcoal	Open burning	Downwind	0.32		Lin et al., 2010a
Rice straw	Open burning	Downwind	0.14	0.33±0.02	Lin et al., 2010b
Sugarcane	Open burning	Downwind	0.15	0.30±0.01	Lin et al., 2010b
Rice straw (M=7.8%)	Open burning	Chamber/hood	0.26±0.03	0.63±0.05	Park and Yu, 2016
Pine needles (M=9.9%)	Open burning	Chamber/hood	0.15±0.04	0.36±0.08	Park and Yu, 2016
Sesame stems (M=10.3%)	Open burning	Chamber/hood	0.29±0.08	0.51±0.08	Park and Yu, 2016

Note: M, DR and RT are the abbreviations of Moisture, Dilution Ratio and Residence Time, respectively.

Reference:

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5. Please comment on other potential primary HULIS source, such as cooking, which might make a contribution, but are not considered in the current model.

Response: We have mentioned other potential primary HULIS source, such as terrestrial and marine emissions, which were not included in these estimations of primary HULIS emissions since they were considered to be negligible for inland cities, such as Beijing (Graber and Rudich, 2006; Zheng et al., 2013).

Cooking contribute about twenty percent of ambient fine organic aerosols in Beijing (Wang et al., 2009; Zhang et al., 2016; Sun et al., 2016). Since cooking emissions was not included in MEIC, and no HULIS emission information about cooking is available, thus cooking are not considered in the current model. It might make a contribution to ambient HULIS and need to be explored in the future.

Graber, E.R. and Rudich, Y.: Atmospheric HULIS: How humic-like are they? A comprehensive and critical review, Atmos. Chem. Phys., 6, 729-753, 2006.

Zheng, G. J., He, K.B., Duan, F.K., Cheng, Y., and Ma, Y. L.: Measurement of humic-like substances in aerosols: A review, Environ. Pollut., 181, 301-314, 2013.

Wang, Q., Shao, M., Zhang, Y., Wei, Y., Hu, M., and Guo, S.: Source apportionment of fine organic aerosols in Beijing. Atmos. Chem. Phys., 9, 8573–8585, 2009.

Zhang, Y. M., Wang, Y. Q., Zhang, X. Y., et al.: Chemical components, variation, and source identification of PM1 during the heavy air pollution episodes in Beijing in December 2016. J. Meteor. Res., 32(1), 1–13, doi: 10.1007/s13351-018-7051-8, 2018.

Sun, Y., Du, W., Fu, P., Wang, Q., Li, J., Ge, X., Zhang, Q., Zhu, C., Ren, L., and Xu, W.: Primary and secondary aerosols in Beijing in winter: sources, variations and processes, Atmos. Chem. Phys., 16 (13), 8309–8329, 2016.

6. Table 2: provide a table footnote to briefly explain the abbreviations for the different residential coals.

Response: we have added a table footnote to briefly explain the abbreviations for the different residential coals.

Note: SM, DT indicate that coals come from the coal mines in ShenMu of Shaanxi Province and DaTong of Shanxi Province in China, respectively. JY and BH were supplied by two companies with the name of JiuYang and BeiHua, respectively, and no producing area of coal were not available. XM indicates briquette coal, which is the abbreviation of briquette coal in Chinese (XingMei).

7. Table S5: add a note to indicate the comparative relationship of this table with Table 3 in the main text.

Response: we have added a note to indicate the comparative relationship of this table with Table 3 in the main text.

Note: only the sources with an average contribution over than 1% were provided. Uncertainty estimation for the seasonal and annual primary and secondary HULISc contributions was determined using a bootstrap sampling technique, which is described in Text S3.2. These uncertainties are based on the assumption that the uncertainty for both $\text{PPM}_{2.5}$ and f_{OC} values are 50%. Uncertainty calculations based on less uncertainties (30% for $\text{PPM}_{2.5}$ and 15% for f_{OC}) are shown in Table 3 in main text.