Anonymous Referee #1

The manuscript is a comprehensive and well-structured study on the potential sources of HULIS, a ubiquitous and abundant atmospheric aerosol constituent. Besides the fact that it is based on a surprisingly extensive experimental setup covering different source measurements and long-term field sampling and observations, it also has a touch of novelty in that identifies residential coal burning as a potentially important yet previously ignored source of primary HULIS. The methodology applied in the manuscript is widely accepted by the aerosol community and its use makes the comparison with the results of other publications feasible. Although the study involves only the analyses of key aerosol constituents such as OC, WSOC, HULIS and inorganics, its conclusions are largely well-founded by the results of the measurements. There are just a few issues that raise some questions in the reviewer.

Response: We thank the reviewer #1 for providing helpful comments and suggestions to improve our manuscript. Below are our responses to reviewer comments including descriptions how we have modified the manuscript.

1) Except for the summer, HULIS are much better correlated with PM2.5 than with OC (Page 8, Line 220 and 224). This is surprising in the light of the fact that HULIS is actually part of OC whereas PM2.5 contains all sorts of other constituents. Not surprisingly, the correlations are the best for WSOC, the closest relative of HULIS. Is there any possible explanation for these observations? Perhaps the effects of vehicular exhaust contributing to OC (and EC) but less to PM2.5 mass concentrations?

Response: Both HULIS and OC are strongly correlated with $PM_{2.5}$, indicating that they have similar sources such as biomass and coal burning, secondary processes. Perhaps the effects of vehicular exhaust contributing to OC (and EC) but less to PM2.5 mass concentrations, which need to explore in the future.

2) In sub chapter 3.2 the differences in HULIS-to-OC ratios of biomass combustion emissions between this study and many other studies around the world are stunning. There are differences by factors of 3–5. The manuscript actually claims that nearly half of the OC are HULIS. Since these are emission measurements on biomass that should not be fundamentally different in different regions (albeit significant differences are seen between various species), there should be something in the experimental setup that causes these unusually high readings. Differences in combustion conditions, dryness of fuel, dilution ratios and excessive cooling may explain these high values. A comparative and critical assessment of the results with those of similar studies would be useful. This is critical since the source apportionment of primary HULIS is based on these emission values.

Response: We summarized the HULISc/OC and HULIS/WSOC values from biomass burning (see the following Table). We think the combustion condition have much influence on the HULIS-to-OC ratios. 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). 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). Dryness content of fuels was found to be not correlated with HULIS-to-OC ratios.

We added a comparative and critical assessment of the results with those of similar studies in the revised manuscript and the following table was added in the supplement.

Summary of HULISc/OC and HULIS/WSOC values from biomass 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 (M=7~14.8%)	Chimney type logwood stove with primary/secondary air	Dilution source sampler with DR=10, RT long enough (no specified)	0.04-0.11		Goncalves et al., 2010
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:

Fan, X., Wei, S., Zhu, M., Song, J., and Peng, P.: Comprehensive characterization of humic-like substances in smoke $PM_{2.5}$ emitted from the combustion of biomass materials and fossil fuels, Atmos. Chem. Phys., 16, 13321–13340, 2016.

Goncalves, C., Alves, C., Evtyugina, M., Mirante, F., Pio, C., Caseiro, A., Schmidl, C., Bauer, H., and Carvalho F.: Characterisation of PM_{10} emissions from woodstove combustion of common woods grown in Portugal, Atmos. Environ., 44(35): 4474-4480, 2010.

Lin, P., Engling, G., and Yu, J.Z.: Humic-like substances in fresh emissions of rice straw burning and in ambient aerosols in the Pearl River Delta Region, China. Atmos. Chem. Phys., 10, 6487-6500, 2010a.

Lin, P., Huang, X.F., He, L.Y., and Yu, J.Z.: Abundance and size distribution of HULIS in ambient aerosols at a rural site in South China, J. Aerosol Sci., 41, 74–87, 2010b.

Park, S. S. and Yu, J.: Chemical and light absorption properties of humic-like substances from biomass burning emissions under controlled combustion experiments, Atmos. Environ., 136, 114-122, 2016.

Schmidl, C., Marr, L. L., Caseiro, A., Kotianova, P., Berner, A., Bauer, H., Kasper-Giebl, A., and Puxbaum, H. Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions, Atmos. Environ., 42, 126–141, 2008a.

Schmidl, C., Bauer, H., Dattler, A., Hitzenberger, R., Weissenboeck, G., Marr, I. L., and Puxbaum, H.: Chemical characterisation of particle emissions from burning leaves, Atmos. Environ., 42, 9070-9079, 2008b.

Lipsky, E. M., and Robinson, A. L.: Effects of dilution on fine particle mass and partitioning of semivolatile organics in diesel exhaust and wood smoke, Environ. Sci. Technol., 40(1), 155-162, 2006.

May, A. A., Levin, E. J. T., Hennigan, C. J., Riipinen, I., Lee, T., Collett, J. L., Jimenez, J. L., Kreidenweis, S. M., Robinson, A. L.: Gas-particle partitioning of primary organic aerosol emissions: 3. Biomass burning, Journal of Geophysical Research-Atmospheres, 118(19): 11327-11338, 2013.

3) I would strongly discourage the application of simple correlations for secondary formation processes (sub chapter 3.4.2). These mechanisms are too complex to be captured by simple regressions: emission fluxes of precursors, rates of transformations, volatilities and water-solubilities of the reaction products, cloud-processing mechanisms, are all different and the processes are strongly non-linear. If, for example, HULIS is not correlated with sulfate, it may also mean that though they are both of secondary origin, the sources and emission fluxes of their precursors are very much different. Therefore lack of correlation does not indicate anything, neither does some moderate virtual correlation. Just think of the examples of sulfate and nitrate, both being secondary aerosol constituents, yet they exhibit completely different formation mechanisms relative to the emissions of their precursors.

Response: we have deleted the sub chapter 3.4.2.

Minor comments:

Typography throughout the manuscript: the improper use of hyphen instead of En dash and Minus characters.

Page 5 Line 122 ’systemis’ . . . space missing

Page 5 Line 122 ’induced’ . . . introduced?

Page 5 Line 124 ’at ambient temperature’ . . .below ambient temperature?

Page 5 Line 142 ’measurements was’ . . .were

Page 6 Line 154 ’determination’ . . . determined

Page 7 Line 198 ’General of ambient’

Page 9 Line 239 ’HULIC’

Page 9 Line 245 Please define ’WSOM’

Response: We revised these grammatical errors accordingly.

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 PM2.5 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 µg m^{-3} (spring), 68 µg m^{-3} (summer), 9 µg m^{-3} (autumn) and 32 µg m^{-3} (winter). In contrast, the averaged $PPM_{2.5}$ on the good performance days are 46 µg m^{-3} (spring), 33 µg m^{-3} (summer), 34 µg m^{-3} (autumn) and 103 µg 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 _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 HULISc/OC for open burning same as biofuel combustion (44%, from our measurement) previously. However, when we compared HULISc/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 HULISc/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:

Fan, X., Wei, S., Zhu, M., Song, J., and Peng, P.: Comprehensive characterization of humic-like substances in smoke $PM_{2.5}$ *emitted from the combustion of biomass materials and fossil fuels, Atmos. Chem. Phys., 16, 13321–13340, 2016.*

Goncalves, C., Alves, C., Evtyugina, M., Mirante, F., Pio, C., Caseiro, A., Schmidl, C., Bauer, H., and Carvalho F.: Characterisation of PM_{10} *emissions from woodstove combustion of common woods grown in Portugal, Atmos. Environ., 44(35): 4474-4480, 2010.*

Lin, P., Engling, G., and Yu, J.Z.: Humic-like substances in fresh emissions of rice straw burning and in ambient aerosols in the Pearl River Delta Region, China. Atmos. Chem. Phys., 10, 6487-6500, 2010a.

Lin, P., Huang, X.F., He, L.Y., and Yu, J.Z.: Abundance and size distribution of HULIS in ambient aerosols at a rural site in South China, J. Aerosol Sci., 41, 74–87, 2010b.

Park, S. S. and Yu, J.: Chemical and light absorption properties of humic-like substances from biomass burning emissions under controlled combustion experiments, Atmos. Environ., 136, 114-122, 2016.

Schmidl, C., Marr, L. L., Caseiro, A., Kotianova, P., Berner, A., Bauer, H., Kasper-Giebl, A., and Puxbaum, H. Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions, Atmos. Environ., 42, 126–141, 2008a.

Schmidl, C., Bauer, H., Dattler, A., Hitzenberger, R., Weissenboeck, G., Marr, I. L., and Puxbaum, H.: Chemical characterisation of particle emissions from burning leaves, Atmos. Environ., 42, 9070-9079, 2008b.

Lipsky, E. M., and Robinson, A. L.: Effects of dilution on fine particle mass and partitioning of semivolatile organics in diesel exhaust and wood smoke, Environ. Sci. Technol., 40(1), 155-162, 2006.

May, A. A., Levin, E. J. T., Hennigan, C. J., Riipinen, I., Lee, T., Collett, J. L., Jimenez, J. L., Kreidenweis, S. M., Robinson, A. L.: Gas-particle partitioning of primary organic aerosol emissions: 3. Biomass burning, Journal of Geophysical Research-Atmospheres, 118(19): 11327-11338, 2013.

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 $PPM_{2.5}$ and f_{OC} values are 50%. Uncertainty calculations based on less uncertainties (30% for $PPM_{2.5}$ and 15% for f_{OC}) are shown in Table 3 in main text.

Quantifying primary and secondary humic-like substances in urban aerosol based on emission source characterization and a source-oriented air quality model

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Abstract: Humic-like substances (HULIS) are a mixture of high molecular weight, water-soluble organic compounds that are widely distributed in atmospheric aerosol. Their sources are rarely studied quantitatively. Biomass burning is generally accepted as a major primary source of ambient humic-like substances (HULIS) with additional secondary material formed in the atmosphere. However, the present study provides direct evidence that residential coal burning is also a significant source of ambient HULIS, especially in the heating season in northern China based on source measurements, ambient sampling and analysis, and apportionment with source-oriented CMAQ modeling. Emissions tests show that residential coal combustion produces 5 to 24% of the emitted organic carbon (OC) as HULIS carbon (HULISc). Estimation of primary emissions of HULIS in Beijing indicated that residential biofuel and coal burning contribute about 70% and 25% of annual primary HULIS, respectively. Vehicle exhaust, industry, and power plants contributions are negligible. Average concentration of ambient HULIS was 7.5 μg/m^3 in atmospheric PM$_{2.5}$ in urban Beijing and HULIS exhibited obvious seasonal variations with the highest concentrations in winter. HULISc account for 7.2% of PM$_{2.5}$ mass, 24.5% of OC, and 59.5% of WSOC, respectively. HULIS are found to correlate well with K$^+$, Cl$^-$, sulfate, and secondary organic aerosol suggesting its sources include biomass burning, coal combustion and secondary aerosol formation. Source apportionment based on CMAQ modeling shows residential biofuel and coal burning, secondary formation are important annual sources of ambient HULIS, contributing ~~57.5~~47.1%, ~~12.3~~15.1%, and ~~25.8~~38.9%, respectively.

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1 Introduction

Humic-like substances (HULIS) are a mixture of higher molecular weight organic compounds that resemble terrestrial and aquatic humic and fulvic acids with similar structures and properties (Graber and Rudich, 2006). HULIS are widely distributed in the atmospheric aerosol, rain, and cloud and fog droplets and account for a significant proportion of the organic carbon and water-soluble organic carbon (WSOC). For example, Zheng et al. (2013) reported that 9% to 72% of WSOC is HULIS. Because of their water-soluble and strong surface-active properties, HULIS may play an important role in the formation of clouds as condensation nuclei, ice nuclei and through aerosol hygroscopic growth (Dinar et al., 2006; Wang and Knopf, 2011; Gysel et al., 2004). Due to their strong light absorption in the UV range, HULIS can play an active role as brown carbon in the radiative transfer and photochemical processes (Hoffer et al., 2006). HULIS deposition can also lead to a decrease in the albedo of ice and snow surfaces (Beine et al., 2011; France et al., 2011; France et al., 2012). Owing to their redox-active characteristics, HULIS was also suggested to induce adverse health effect (Lin and Yu, 2011; Ghio et al., 1996; Verma et al., 2012).

In recent years, studies focusing on the spatial and temporal variations, sources, and formation of HULIS have been reported. A summary of these studies is provided in Table S1. Previous studies have identified primary emission and atmospheric secondary formation as the important sources of HULIS. Among the primary emission sources, biomass burning is generally accepted as a major source of HULIS, with the evidence from ambient and source sampling as well as source apportionment studies (Lin et al., 2010a, b; Kuang et al., 2015; Park and Yu, 2016; Schmidl et al., 2008a, b; Goncalves et al., 2010). Recently, residential coal burning was suggested as an important primary HULIS source during winter (Tan et al., 2016; Voliotis et al., 2017). However, direct evidence of HULIS emission from coal combustion is limited. Only one study on HULIS emitted from residential coal combustion was reported and the results showed that HULIS accounted for 5.3% of smoke $PM_{2.5}$ (Fan et al., 2016). Unfortunately, only a light coal in the shape of honeycomb briquette was tested that did not reflect the variety of coal types and forms actually being used for residential heating and cooking in China. Another possible primary HULIS source is vehicle exhaust although there is uncertainty in the importance of this source (El Haddad et al., 2009; Salma et al., 2007; Lin et al., 2010b; Kuang et al., 2015). No direct evidence of primary HULIS in vehicle exhaust has been reported. Secondary processes, including formation in the cloud droplets, heterogeneous or aerosol–phase reactions, can be important sources of HULIS (Lin et al., 2010b; Zheng et al., 2013).

Previous studies of HULIS source identification were generally based on the relationship between HULIS and the tracers for specific sources (such as K, levoglucosan, Cl^-, etc.) (Voliotis et al., 2017; Tan et al., 2016; Lin et al, 2010;

Park and Son, 2016; Baduel et al., 2010). Those correlation analyses between HULIS and some species may provide some information regarding possible source and formation of HULIS. However, they do not provide quantitative source apportionments. To date, studies that quantitatively identify HULIS sources are limited (Kuang et al., 2015; Srivastava et al., 2018). Kuang et al. (2015) applied positive matrix factorization (PMF) to apportion sources of ambient HULIS in the Pearl River Delta (PRD) in Southern China. Their study showed that secondary formation was the most important source of HULIS throughout the year with an annual average contribution of 69% at an urban site. Biomass burning also contributed significantly to ambient HULIS.

Thus, information is scarce on the quantitative apportionment of HULIS sources in the more polluted regions in Northern China, especially in the winter when large quantities of coal are consumed for indoor heating. Moreover, a considerable proportion of coal is burned in residential household stoves in rural, suburban and even some urban areas under poor combustion conditions and without any emission controls. This coal combustion results in high air pollutant emissions and high ambient concentrations. Wang et al. (2016) estimated that more than 30 million tons of coal are burned per year in households in just the Beijing, Tianjin, and Hebei (BTH) region in Northern China. Residential sources in the BTH region contributed to 32% and 50% of primary $PM_{2.5}$ emissions over the whole year and in winter, respectively (Liu et al., 2016).

The primary goals of this study are to determine whether residential coal combustion is a significant source of ambient HULIS and quantify its contributions to HULIS in Beijing. Given the large vehicle population in Beijing (up to 5.2 million in 2012), this study also provides a chance to examine the vehicular emissions contribution to ambient HULIS. Studies included: (1) Characterization of the HULIS emitted from residential coal stoves, vehicle exhaust, and residential biofuel burning; (2) Estimation of anthropogenic primary emission of HULIS based on these source measurements; (3) Measurement of HULIS concentrations and other major species in the ambient urban Beijing $PM_{2.5}$ from June 2012 to April 2013; and (4) Application of the source-oriented Community Multiscale Air Quality (CMAQ) model to quantitatively determine the source contributions to HULIS. The information obtained in this study improves our understanding of the characteristics and sources of primary HULIS and the impact of those sources on HULIS in ambient $PM_{2.5}$.

2 Materials and Methods

2.1 Ambient sampling

Beijing is surrounded by mountains to the west, north, and northeast, and is adjacent to the northwest portion of the North China Plain. It has a warm and semi-humid continental monsoon climate with four distinctive seasons, characterized by strong windy and dusty weather in spring, high temperatures and humidity with extensive rain in summer, cool and pleasant weather in autumn, and cold and dry weather in winter. The annual average wind speed is 2.5 m s^{-1} with mostly northerly or northwesterly winds in winter and southerly or southeasterly winds in summer. Twenty-four-hour ambient $PM_{2.5}$ samples were collected non-continuously from 14 June 2012 to 2 April 2013 on the campus of Beihang University (BHU, 39°59'N, 116°21'E) (Figure S1). The sampling period covered four seasons with 132 samples being collected for HULIS analysis. The site is surrounded by educational and residential districts without major industrial sources. Major nearby roads are the North Fourth Ring Road about 900 m to the north, North Third Ring Road about 1.2 km to the south, and Xueyuan Road about 350 m to the east. Ambient $PM_{2.5}$ sampling instruments were installed on the roof of a building approximately 25 m above the ground level at Beihang University. A high-volume aerosol sampler (RFPS-1287-063, Thermo, USA) was operated at a flow rate of 1.13 m^3 min^{-1} to collect $PM_{2.5}$ samples on prebaked quartz filters (with area 417.6 cm^2) for the determination of water-soluble organic carbon (WSOC) and humic-like substances (HULIS). $PM_{2.5}$ samples were also collected using a 5-channel Spiral Ambient Speciation Sampler (SASS, Met One Inc., USA) with a flow rate of 6.7 L min^{-1}. Wang et al. (2015) provided the details of the sample collection.

Meteorological data including wind speed (WS), temperature, relative humidity (RH) and precipitation were obtained from China Meteorological Data Sharing Service System (http://cdc.cma.gov.cn/home.do).

2.2 Source Sampling

Residential biofuel and coal combustion emissions, and vehicle exhaust, which are representative of typical emission sources around Beijing, were sampled in this study.

2.2.1 Residential biofuel and coal combustion

Three typical types of biofuel, i.e. wheat straw, corn stover, and wood, were burned in an improved stove, which has an enclosed combustion chamber and a bottom grate and a chimney. The sampling procedures are described by Li et al. (2007, 2009) and are briefly summarized here. The water boiling test was used to simulate a common cooking procedure. The burning cycle included heating a specific amount of water from room temperature to its boiling point and then letting it simmer for a few minutes. Both the high power and low power phases were included in the burn cycle to simulate cooking practices of a typical household. The sampling period covered the entire cycle and lasted 20-30 minutes.

Five coal types were selected for source testing covering a wide range of maturity with volatile matter content varying from 9.6% to 32.4%. Two coal stoves were tested, including a high efficiency, heating stove that employs under-fire combustion technology and a traditional cooking and heating stove that employs over-fire combustion technology (Li et al., 2016). Four chunk coals and one briquette coal were burned in the high efficiency stove and three chunk coals were burned in the traditional stove. Coal/stove combinations are presented in Table 2. To reduce the interference from igniting the fire, coal was ignited with a propane gas flame from a torch. Emission sampling covered from fire start to fire extinction and lasted two to three hours.

Source testing of residential biofuel and coal combustion was performed at Beihang University. The test fuels were air-dried, and the results of their proximate and ultimate analyses are listed in Table ~~S1~~ S2 in Supplement~~I~~. An outline of the sampling system is shown in Fig. S2. The stove was placed into a chamber. Purified air was introduced into the chamber with a fan to provide dilution air. Emissions were extracted from the chimney with an exhaust hood and were diluted with purified air, cooled to no more than 5 degrees Celsius at ambient temperature, and then drawn through a sampling duct and exhausted from the laboratory. Both air flows were adjusted using frequency modulators to change fan speeds. The gas flow velocity in the sampling duct was measured by a pitot tube to be over 5 m/s. Flow was isokinetically withdrawn from the sampling duct with a probe and directed into the residence chamber. $PM_{2.5}$ samples were collected from the end of the residence chamber onto prebaked quartz filters with a diameter of 47mm through $PM_{2.5}$ cyclones at a flow rate of 16.7 liters/min.

2.2.2 Vehicle exhaust

Four light-duty gasoline vehicles certified as meeting the China 4 emissions regulations were tested for their emissions on a chassis dynamometer. The tests were conducted using the New European Driving Cycle (Marotta, et al., 2015) and lasted 1180 s, including four repeated urban driving cycles and one extra-urban driving cycle. The emissions testing and sampling system are described in detail by Li et al. (2016) and are briefly summarized here. The vehicle exhaust was directed into a critical flow Venturi constant volume sampler in a full flow dilution tunnel. The $PM_{2.5}$ samples were collected on prebaked quartz filters with a diameter of 47mm through $PM_{2.5}$ cyclones at a flow rate of 80 L/min.

Three heavy-duty diesel trucks were selected to perform on-road emission test. The tests were conducted on both highway and city roads. The emission testing and sampling system are described in detail elsewhere (He et al., 2015) and are briefly summarized here. A Micro Proportional Sampling System (SEMTECH-MPS; Sensors Inc., MI, USA) was used to draw a constant ratio of sample flow from exhaust and dilute the sample flow. $PM_{2.5}$ samples were collected onto prebaked quartz filters with a diameter of 47mm through $PM_{2.5}$ cyclones at a flow rate of 10 liters/min.

Tunnel measurements were~~as~~ also conducted to collect vehicle exhaust at the Badaling Tunnel in Beijing. The length of the tunnel is 1085 m. The ventilation in the tunnel was achieved by the flow of the traffic induced into the tunnel during the sampling period. $PM_{2.5}$ samplers with prebaked 47mm quartz filters were operated at a flow rate of 16.7 L/min at the inlet and the outlet of the tunnel simultaneously. The sampling period was 2 hours and the samples represent the mixed exhaust of gasoline-fueled vehicles and diesel-fueled vehicles.

All source samples collected on the quartz filters were analyzed for HULIS, WSOC and OC/EC according the methods described in Section 2.3.

2.3 Chemical Characterization

HULIS isolation was based on the extraction method developed by Varga et al. (2001) and used in many other studies (Nguyen et al., 2014; Lin et al., 2010b; Fan et al., 2012; Song et al., 2012; Lin et al., 2011; Salma et al., 2013; Feczko et al., 2007; Krivácsy et al., 2008). The separation procedure is provided in ~~SI~~ Text S1 of Supplement. WSOC and $HULIS_C$ were determined using a total organic carbon (TOC) analyzer (Shimadzu TOC-Vcph, Japan) based on a combustion-oxidation, non-dispersive infrared absorption method. The TOC was determined~~ation~~ by subtracting inorganic carbonate (IC) from total carbon (TC): TOC = TC - IC. The reported data were the average results of three replicate measurements. Mass concentrations of HULIS were obtained from $HULIS_C$ by multiplying a scaling factor of 1.9 as suggested by Lin et al. (2012a), Kiss et al. (2002), and Zheng et al. (2013).

A 0.5 cm^2 punch from each quartz filter was analyzed for OC and EC using a DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, USA) following the IMPROVE-A thermal optical reflectance (TOR) protocol (Chow et al., 2007).

The $PM_{2.5}$ samples from SASS were also analyzed for mass, water-soluble inorganic ions analysis as described by Wang et al. (2015).

2.4 CMAQ modelling of primary HULISc

A source-oriented version of the Community Multiscale Air Quality (CMAQ) model (version 5.0.1) was used in this study to track primary $PM_{2.5}$ ($PPM_{2.5}$) from different emission sectors and determine the resulting concentrations of primary HULIS. The model was used in a previous study to determine source contributions to $PPM_{2.5}$ mass, EC and primary OC (POC) in China. Details of the source apportionment technique can be found in Hu et al (2015). In summary, source contributions to $PPM_{2.5}$ mass were directly determined using non-reactive source-specific tracers to track the emissions of $PPM_{2.5}$ from different sources. These non-reactive tracers were treated identically to the other PPM components when simulating their emission, transport, and removal. A constant scaling factor (typically 10^{-4} or 10^{-5}) was used to scale the actual emission rate of these tracers to ensure that their concentrations are sufficiently low that they do not alter the removal rates of other PM components. The concentrations and source contributions to EC and POC were determined during post-processing by using source-specific emission factors as well as the model predicted source contributions to $PPM_{2.5}$ mass concentrations. This technique can be used to determine source contributions to primary HULIS. For example, contributions of the i^{th} emission source to primary HULISc concentration ($HULISc_{,i}$) can be calculated using equation (1):

$$HULISc_{,i}=PPM_{2.5,i}*f_{OC,i}*f_{HULIS,i} \qquad (1)$$

where $f_{HULIS,i}$ is the mass fraction of HULIS per unit emission of POC from the i^{th} source (see Section 3.3 below for estimation of HULIS primary emission) and $f_{OC,i}$ is the mass fraction of POC per unit emission of $PPM_{2.5,i}$ from the i^{th} source, and $PPM_{2.5,i}$ is the calculated source contributions to $PPM_{2.5}$ from the i^{th} source based on the non-reactive tracer. The total concentration of primary HULIS can be determined by adding the primary HULIS contributions from the different sources.

In this study, the model uses a 36 km × 36 km horizontal resolution to cover a rectangular domain that includes all of China and neighboring countries. Source contributions to HULIS were calculated for the periods when observations of HULIS are available. Emissions from anthropogenic source sectors (residential sources, power plants, industries, and transportation) are based on Multi-resolution Emission Inventory of China (MEIC) 2012 (www.meicmodel.org). Open biomass burning was estimated using the FINN dataset from the National Center for Atmospheric Research (NCAR) (Wiedinmyer et al., 2011). Natural emissions from soil erosion and sea spray were modeled within the CMAQ model (Appel et al., 2013; Kelly et al., 2010). Biogenic emissions were estimated using the Model for Emissions of Gases and Aerosol from Nature (MEGAN) version 2.10. Meteorological fields were calculated using the Weather Research and Forecasting (WRF) model. Details of the model setup, input data preparation, as well as model evaluation for $PPM_{2.5}$ mass are documented by Hu et al (2015). In this study, a comparison of predicted daily $PPM_{2.5}$ concentrations with observations was performed and only those predictions with fractional errors (FE) less than 0.6 were included in the calculation of primary HULIS. The values of f_{OC} for different source sectors used in the calculation are included in ~~SI~~ Table ~~S3~~S4 of Supplement. These values were used in Ying et al. (2018), and the predicted daily-average POC and EC concentrations generally agree with predictions for both daily and annual average concentrations.

3 Results and discussion

3.1 General of ambient aerosol characteristics

The concentrations of $PM_{2.5}$, carbonaceous species (OC, EC, WSOC and HULIS), and inorganic ions such as SO_4^{2-}, NO_3^-, NH_4^+, and K^+ are summarized in Table 1. The 24-hour average $PM_{2.5}$ concentration for the sample set was 106 ± 89 μg/m^3, about three times the national annual air quality standard (35 μg/m^3). The highest concentration (~600 μg/m^3) appeared on 12-13 January 2013 as reported in other studies (Quan et al., 2014; Tian et al., 2014; Zheng et al., 2015).

The severe pollution events were always accompanied by high relative humidity and low wind speeds (Fig. 1). During the entire sampling period, severely polluted days (PM$_{2.5}$ concentrations ≥ 150 µg/m^3) constituted about 22%, while fair days (PM$_{2.5}$ concentrations ≤ 75 µg/m^3) approached 50%. The average PM$_{2.5}$ concentrations in summer, autumn, winter, and spring were 98 ± 60 µg/m^3, 58 ± 48 µg/m^3, 150 ± 121 µg/m^3, and 120 ± 76 µg/m^3, respectively.

The average HULIS concentration for the study period was 7.5 ± 7.8 µg/m^3. This value is lower than the average value of 11.8 µg/m^3 measured at a rural site in the PRD region that was heavily influenced by biomass burning (Lin et al., 2010b). However, it is higher measurements in the urban areas (about 5 µg/m^3) in the PRD (Lin et al., 2010a; Kuang et al., 2015), urban Shanghai (about 4 µg/m^3) (Zhao et al., 2015), and urban Lanzhou (about 4.7 µg/m^3) (Tan et al., 2016). HULIS exhibited obvious seasonal variations as shown in Figure 1 and Table 1. The seasonal average concentrations were 5.5 ± 4.4 µg/m^3, 5.6 ± 4.7 µg/m^3, 12.3 ± 11.7 µg/m^3, and 6.5 ± 5.5 µg/m^3 in summer, autumn, winter, and spring, respectively. The winter mean was about twice the value in any other season, and the highest concentration (54.96 µg/m^3) of HULIS was observed on the same day that the highest concentration of PM$_{2.5}$ was observed. The mean HULIS concentrations were very similar between summer and autumn in contrast with PM$_{2.5}$ that has much higher concentrations in the summer (Table 1). These seasonal variations were similar with those observed in Aveiro and K-puszta (Feckzo et al., 2007), but those annual average concentrations (about 2.4 µg/m^3 and 3.2 µg/m^3, respectively) were much lower than in Beijing. The concentrations of HULIS in previously reported studies are summarized in ~~Supporting~~ Table S1 of Supplement.

HULIS and PM$_{2.5}$ had a significant positive correlation with the annual r^2=0.90 (r^2 = 0.77, 0.96, 0.96 and 0.94 in summer, autumn, winter, and spring, respectively) (Figure S4a). The seasonal average of HULIS/PM$_{2.5}$ was 5.9%, 9.4%, 7.9%, and 4.8% in summer, autumn, winter, and spring, respectively. The annual average of HULIS/PM$_{2.5}$ was 7.2% ± 3.3%, lower than the ~10% in the PRD region (Lin et al., 2010a).

Strong correlations of HULIS$_C$ with OC were observed with the annual r^2=0.87 (r^2 = 0.94, 0.82, 0.89 and 0.84 in summer, autumn, winter, and spring, respectively) (Fig S4c). The percentage of HULIS$_C$ in OC for summer, autumn, winter, and spring, respectively, were 29.2 ± 6.2%, 26.2 ± 9.6%, 21.0 ± 7.1%, and 22.0 ± 6.9% with an annual average of 24.5% ± 8.3%.

Strong correlations of HULIS$_C$ with WSOC were also observed with the annual r^2=0.98 (r^2 = 0.99, 0.96, 0.99 and 0.98 in summer, autumn, winter, and spring, respectively) (Figure S4b). The percentage of HULIS$_C$ in WSOC for summer, autumn, winter, and spring, respectively, were 66.7 ± 5.4%, 54.1% ± 11.2%, 62.3% ± 5.7% and 56.6% ± 6.3% with an annual average of 59.5% ± 9.2%, suggesting that HULIS$_C$ was the major constituent of WSOC. This value is comparable to the results (about 60%) at urban sites in the PRD region (Lin et al., 2010b; Fan et al., 2012), Shanghai

(Zhao et al., 2015), Korea (Park et al., 2012), Budapest (Salma et al., 2007; 2008; 2010), and high-alpine area of the Jungfraujoch, Switzerland (Krivácsy et al., 2001). However, it is higher than the rural areas in K-puszta, Hungary (Salma et al., 2010) and the northeastern US (Pavlovic and Hopke, 2012). The ratios of $HULIS_C$/WSOC reported by previous studies are listed in ~~Supporting~~ Table S1 of Supplement.

3.2 HULIS emission characteristics from various sources

The measured $HULIS_C$/OC (i.e. $f_{HULIS,i}$), $HULIS_C$/WSOC from the source samples are presented in Table 2. Biomass combustion produces a significant fraction of ~~HULIC~~ HULIS in OC (0.41-0.50) whether burning wood or crop straw. Those values are high compared to previous studies (see Table S3 of Supplement). The $HULIS_C$/OC values obtained by Lin et al., (2010a, 2010b) were 0.14 to 0.34 from rice straw and sugarcane open burning in the PRD region in south China. Park and Yu (2016) found the ratios from open burning rice straw, pine needles, and sesame stems in Korea were in the range of 0.15 to 0.29. Schmidl et al. (2018a, 2018b) reported the ratios of 0.01-0.12 for wood burned in the stove~~ing~~ and 0.33-0.35 for leaves open burning in the mid-European Alpine region. Goncalves et al. (2010) obtained ratios of 0.04 to 0.11 from wood burned in the stove~~ing~~ in Portugal. HULIS is an important component of water soluble organic matter (WSOM). High $HULIS_C$/WSOC ratios (0.62 to 0.65) were observed for three types of biomass burning in this study. These results are comparable with two previous studies. Fan et al. (2017) reported the ratios from open burning rice straw, corn straw, and pine branch were in the range of 0.57 to 0.66. Park and Yu (2016) obtained ratios in the range of 0.36 to 0.63 from open burning three types of biomass. However, Lin et al. (2010a) reported relatively low values ranging from 0.30 to 0.33 from open burning rice straw and sugarcane ~~burning~~. Possible influence factors to $HULIS_C$/OC ratios were summarized in Table S3 of Supplement. Combustion condition have much influence on the HULIS-to-OC ratios. 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). 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). Dryness content of fuels was found to be not correlated with HULIS-to-OC ratios.

Residential coal combustion produces 5 to 24% of the OC as HULIS for all the coal/stove combinations in this study. Only one prior study measured HULIS emitted from residential honeycomb coal briquette combustion (Fan et al., 2016). However, the HULIS to OC ratio was not reported in that study. HULIS/WSOM ratio (0.46) in that study are comparable with our $HULIS_C$/WSOC data (0.41-0.62).

Light-duty gasoline and heavy-duty diesel vehicles also produced primary HULIS on the order of 5 to 16% of the emitted OC. The HULIS content detected in the vehicle exhaust samples was generally less than the detection limit for these measurements. Thus, these reported ratios of $HULIS_C$ to OC for vehicle emissions have high uncertainties. Ratios of $HULIS_C$ to OC for vehicle emissions obtained in this study are much higher than prior tunnel measurements (2-5%) (El Haddad et al. 2009). However, they are comparable with those from residential coal combustion. Due to more complete combustion or more advance emission controls in vehicles than residential solid fuel combustion, OC emission factors for vehicles are normally around two orders of magnitude less than that for residential coal combustion (MEP of China, 2014), so HULIS emission from vehicles can be neglected as described in Section 3.3.

3.3 Estimation of HULIS primary emission

The average values of $f_{HULIS,i}$ for residential biofuel and coal combustion, and vehicle exhaust obtained from our measurement were used for to assess the extent of primary emissions. Due to lack of $f_{HULIS,i}$ for the other sectors, such as power plants and industries, considering combustion/production technology and emission control technology, we assumed values for these two sectors as 0.01 and 0.05, respectively.

Based on OC emissions for different sources in the MEIC inventory and the $f_{HULIS,i}$ for the various sources described above, the annual anthropogenic primary emission of HULIS in Beijing is estimated to be approximately 6.3 Gg with over 60 percent of this primary HULIS being emitted during the heating season. Residential biomass and coal burning contribute about 70% and 25% of the annual primary HULIS emissions, respectively. Vehicle exhaust contributions to annual primary HULIS emission are negligible (less than 2%). While industry sector and power plants contribute about 3% and close to zero, respectively. In winter, residential biomass and coal burning contribute close to 98 percent of primary HULIS (~~Supporting~~ Table ~~S3~~S5 of Supplement).

Terrestrial and marine emissions 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.

3.4 Possible primary sources ~~and secondary formation~~ of HULIS

Ambient HULIS sources include primary sources and atmospheric secondary processes that convert gaseous precursors to HULIS. The correlation between HULIS and other measured constituents provide information regarding possible sources and formation mechanisms of HULIS.

~~3.4.1 HULIS from primary sources~~

Correlations between HULIS and primary species in $PM_{2.5}$ are shown in Figure 2. POC and secondary organic carbon (SOC) were estimated using the EC tracer method (Lim and Turpin, 2002; Turpin and Huntzicker, 1995). The details of the method and evaluation are provided in Text S2. Figures 2a and 2b show that there are strong correlations between HULIS and POC, and HULIS and EC throughout the year indicating that HULIS has sources and/or transport processes similar to those of POC and EC. Both POC and EC are co-emitted by the incomplete combustion of carbon-containing fuels. According to the 2010 MEIC data for Beijing 2010, biomass and residential coal burning contribute more than 80 percent of the POC emissions, the industrial sector contributes over 10 percent, and vehicular exhaust contributions are negligible. For EC emission, residential coal burning contributes more than 50 percent, biomass burning, industry, and vehicles contributes the rest.

K^+ generally originate from biomass burning with lesser contributions from coal burning and dust. However, biomass burning is regarded as the most important source for K^+ and it is often used as an indicator of biomass burning (Kuang et al., 2016; Zhang et al., 2013; Park et al., 2015; Pio et al., 2008; Wang et al., 2011; 2012; Cheng et al., 2013). In North China, biomass burning occurred in all seasons including residential cooking, heating, and open biomass burning (Cheng et al., 2013; Zheng et al., 2015). High K^+ concentrations in this study were observed with mean values of 2.2 ± 2.9 $\mu g/m^3$, 1.3 ± 1.0 $\mu g/m^3$, 3.2 ± 3.6 $\mu g/m^3$ and 2.2 ± 1.3 $\mu g/m^3$ in summer, autumn, winter, and spring, respectively, and an annual average of 2.2 ± 2.6 $\mu g/m^3$. As shown in Figure 3c, HULIS and K^+ exhibited a strong correlation with r^2=0.76, 0.73, and 0.61 in summer, autumn, and spring, respectively, suggesting the contribution of biomass burning to HULIS. During the winter sampling period, a low correlation was initially obtained ($r^2 = 0.21$). However, two extreme values of K^+ were observed on New Year's Eve (February 9, 2013, 14.6 $\mu g/m^3$) and Lantern Festival (February 24, 2013, 17.6 $\mu g/m^3$). Prior studies had suggested that fireworks during the Spring Festival and Lantern Festival produce very high K^+ concentrations (Shen et al., 2009; Jing et al., 2014; Jiang et al., 2015). Excluding these two days (red points in Figure 2c), the correlation between HULIS and K^+ increased to r^2=0.73, indicating the contribution of biomass burning to HULIS in winter. The strong correlation coefficient between HULIS and K^+ across all the seasons also confirmed that biomass burning was a significant primary HULIS emission source as presented in the Section 3.3.

Cl^- is usually believed to be associated with coal combustion and biomass burning (Yu et al., 2013; Gao et al., 2015; Yao et al., 2002; Li et al., 2007; Li et al., 2009). A significant contribution from sea-salt particles for Cl^- in $PM_{2.5}$ can be excluded since the average mole ratios of Cl^- to Na^+ across four seasons in this study is 5.0, much higher than the ratio in seawater of 1.17. Moreover, the sampling site in Beijing is about 200 Km from the sea. The correlation of HULIS and Cl^- is shown in Fig. 2d. In winter and spring, HULIS is moderately correlated with Cl^- with r^2=0.56 and r^2=0.64, respectively. While weaker correlations were observed in summer and autumn with r^2=0.40 and r^2=0.43, respectively. This result reflects the different amounts of coal burned in specific seasons. In winter and spring in northern China, coal combustion for heating was quite prevalent and more coal was burned compared to the other two seasons, resulting in the substantial emissions of gaseous and particulate pollutants, including HULIS and Cl^-. ~~The source study in Section 3.2 found that HULIS contributed to about 12% of OC emitted from residential coal combustion.~~ The correlation coefficient between HULIS and Cl^- in winter and spring provides additional support for coal burning being an important primary HULIS emission source as discussed in Section 3.3. The strong correlation between HULIS and Cl^- in winter (R^2=0.89) and weak correlation in summer (R^2=0.17) were also revealed in Lanzhou, another city in northern China (Tan et al., 2016). Significant correlation between HULIS and Cl^- in wintertime urban aerosols from central and southern Europe were also found (Voliotis et al., 2017). The authors suggest the high concentration of HULIS during winter was probably related with residential coal burning (Tan et al., 2016; Voliotis et al., 2017).

Ca^{2+} would be more likely originated from the re-suspended road dust and long-range transported dust (Gao et al., 2014). The poor correlation between HULIS and Ca^{2+} (as shown in Figure 2e) indicated dust was not likely to be an important source of HULIS.

~~3.4.2 HULIS associated with atmospheric secondary processes~~

~~The correlations between HULIS and related secondary species are shown in Figure 3. As shown in Figure 3a and 3b, HULIS correlated well with SO_4^{2-} and SOC (R^2=0.68 for HULIS and SO_4^{2-} and R^2=0.61 for HULIS and SOC), suggesting that HULIS and secondary species may have similar formation pathways. Moderate to strong correlations of HULIS and SO_4^{2-}, and HULIS and SOC were observed in autumn and winter, but with significant differences in the concentrations. The lower temperature and solar intensity in winter were not conducive to the photochemical formation of secondary aerosols, but high relative humidity and stable synoptic meteorological conditions accompanied with heterogeneous reactions probably played a role in the formation of secondary aerosols (Zheng et al., 2015). In summer, HULIS was strongly correlated with SOC (R^2=0.85), while weakly correlated with SO_4^{2-} (R^2=0.41), indicating the distinct formation processes of HULIS and SO_4^{2-}. High temperature and solar radiation accelerated the photochemical reactions between oxidants and organic precursors (Lin et al., 2010). However, a moderate correlation of HULIS & SO_4^{2-} (R^2=0.36) but unfavorable correlation between HULIS and SOC (R^2=0.10) were acquired in spring, suggesting the different formation pathways of HULIS and SOA.~~

3.5 HULIS source apportionment based on CMAQ modelling

CMAQ predicted concentrations of $PPM_{2.5}$ from different sources were used to calculate HULISc from these sources using equation (1). The total concentration of primary HULIS can be determined by adding up primary HULIS from different sources. Figure ~~4~~ 3 shows the predicted primary HULISc and observed HULISc concentrations with the prediction uncertainty. Only days with acceptable $PPM_{2.5}$ performance were shown in the Figure ~~4~~3. Primary HULISc in January and March 2013 accounts for almost all observed HULISc in these two months. In summer and autumn 2012, predicted primary HULISc concentrations are approximately 1-2 μg m^{-3}. There were days when the observed HULISc concentrations were much higher than predicted primary HULISc concentrations indicating potential contributions of secondary HULISc.

Table 3 shows the seasonal contributions for each source as well as average source contributions for the whole sampling period to ambient HULIS in Beijing based on the observed total HULISc and CMAQ predicted primary HULISc on the days with acceptable $PPM_{2.5}$ performance. Contributions of HULISc from secondary processes were determined by subtracting predicted primary HULISc from observed HULISc. For those days when the predicted primary HULISc concentrations are greater than the observed HULISc, the predicted primary HULISc concentrations were set to equal the observed HULISc and the secondary HULISc were set to zero. Based on the HULIS emissions from residential biofuel and coal burning described in Section 3.3, the contributions of biofuel and coal burning in the residential sector to ambient HULIS were estimated separately.

Overall, residential biofuel burning was the most important source of ambient HULIS, contributing ~~more than~~nearly half of the ambient HULIS concentrations, much higher than those results from the PRD in Southern China (less than 20%) (Kuang et al. 2015). This difference is likely with the result of greater biofuel burning during the heating seasons in the Beijing area. Residential coal burning contributes ~~12.3±2.8~~15.1±2.9% to ambient HULIS and is also a significant source of ambient HULIS. A large contribution from residential sector to ambient HULIS is consistent with the estimation of HULIS primary emission and the correlations between HULIS and primary species previously presented. Vehicle emissions and other primary sources, such as industries, contribute negligible amounts to the ambient HULIS. Contributions from the residential sector display strong seasonal variations. In winter and spring, residential biofuel and coal burning accounted for ~~over~~ about 80% of the total HULISc while their contributions were reduced to approximately 40% in summer and autumn. The seasonal variations were a reflection of seasonal pattern of those activities in this region.

Secondary formation is estimated to have contributed an average of ~~25.8±9.3~~38.9±9.1% to the HULIS concentrations and was another major source to ambient HULIS~~ as indicated by the correlations between HULIS and secondary species (i.e. SNA, SOC)~~. However, our result is much lower than those results from PRD in Southern China (55 to 69%) (Kuang et al. 2015). The difference is driven by the differences in sources and climatological patterns between these two sites. There is much greater combustion for space heating in the colder north and atmospheric reaction rates will be higher in the warmer south. Contributions from secondary processes also show obvious seasonal variations trend. In winter and spring, secondary processes accounted for ~~less than~~ 25% to ~~20~~30% of the total HULISc with large uncertainties while their contributions were increased to ~~40±18~~50.2±19.3% and ~~53±17~~63.2±18.3% in summer and autumn. Higher secondary contributions were also found during warm seasons in the PRD region (Kuang et al. 2015). In addition to the proposed heterogeneous secondary formation pathways for HULISc, oxidation reactions initiated by chlorine (Cl) radicals can form SOA (Wang and Ruiz, 2017; Riva et al., 2015). Thus, Cl release by coal combustion may have the potential to contribute to HULISc, especially during winter when OH radical concentrations are much lower (monthly average 5.5×10^{-3} ppt for winter vs. 1.25×10^{-1} ppt for summer based on CMAQ calculations for Beijing). However, the concentrations of secondary HULISc for winter estimated in this study are uncertain (1.8 ± 2.2 μg m^{-3}) compared to the summer time average concentration (1.0 ± 0.4 μg m^{-3}). Therefore, the role of Cl initiated reactions producing HULISc cannot be definitively determined.

Figure ~~5~~ 4 shows scatter plot of predicted primary HULISc vs observed HULISc concentrations. Moderate to strong correlations between predicted primary HULISc were observed in winter and spring, while relatively weaker correlations were found in autumn. Moreover, low correlations were observed in summer. The variation of correlation coefficient between predicted primary HULISc and observed HULISc in different seasons also provides additional support for the relative importance of primary and secondary HULIS as shown in Table 3.

Supporting Information

The supporting information file for this paper provides the details of HULIS analytical procedures, and prior literature regarding HULIS in the ambient aerosol. It also provides some additional figures and descriptions that help to support the analyses and discussion presented in the paper.

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Figures

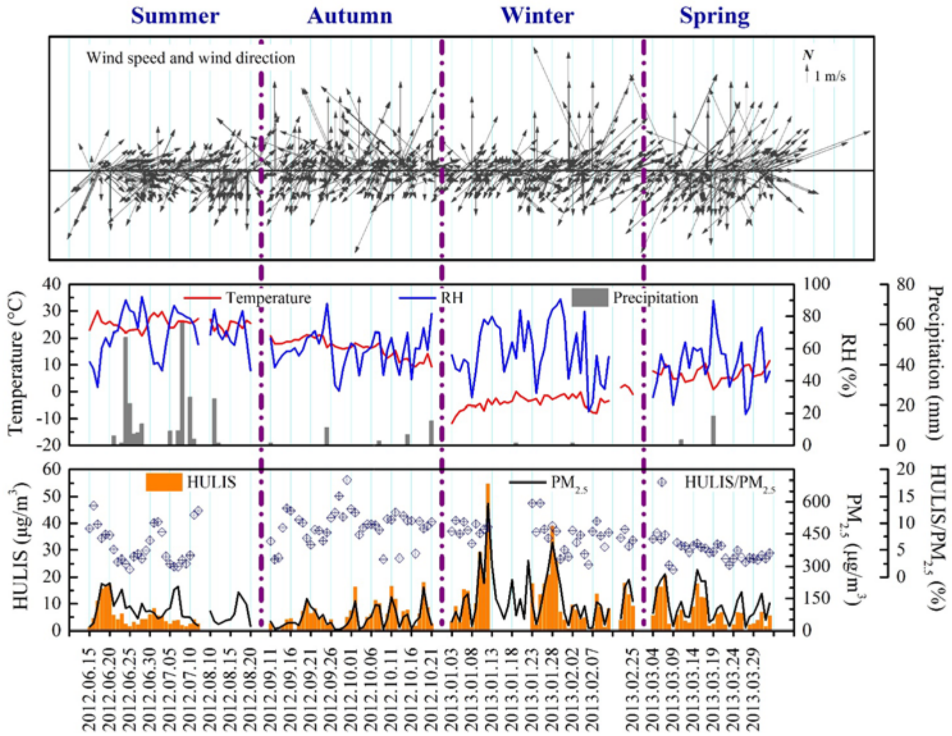


Figure 1. Time series of meteorological data (wind speed, wind direction, temperature, relative humidity and precipitation), HULIS, $PM_{2.5}$ and HULIS/$PM_{2.5}$ for the sampling period.

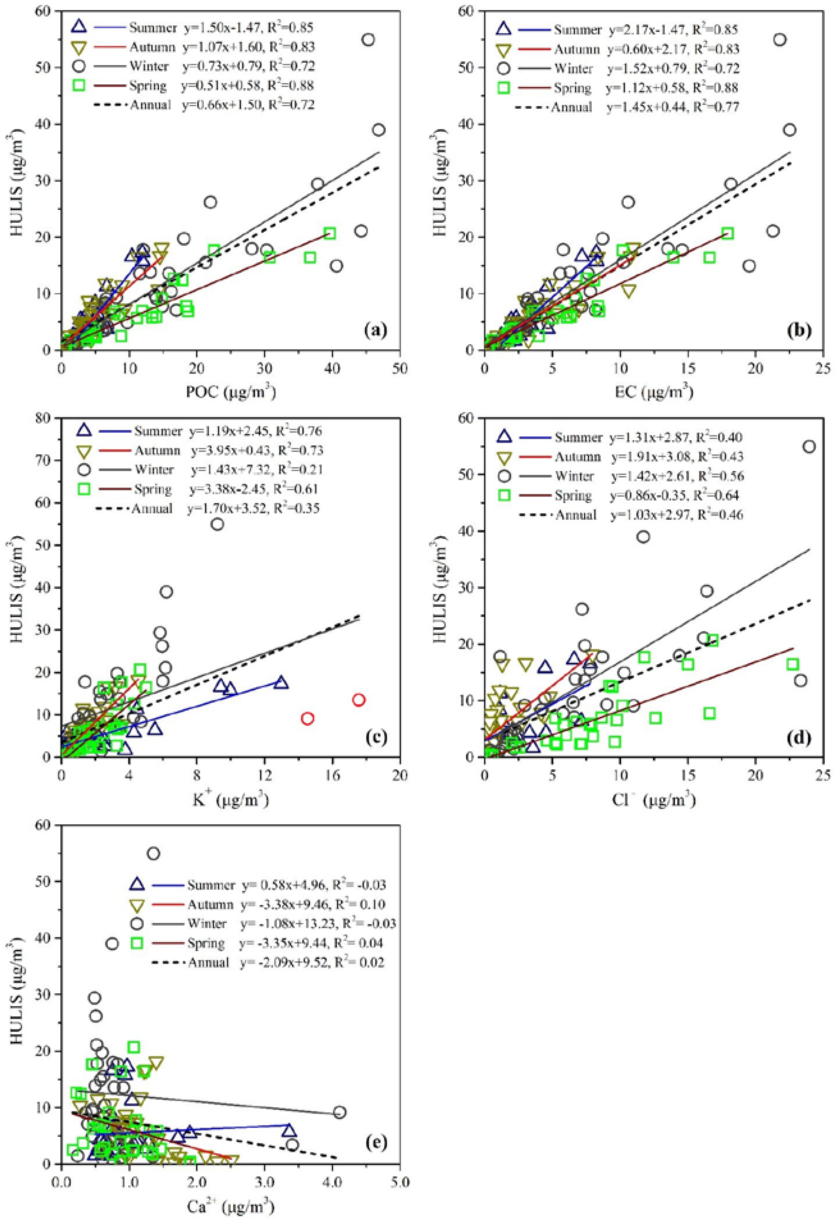
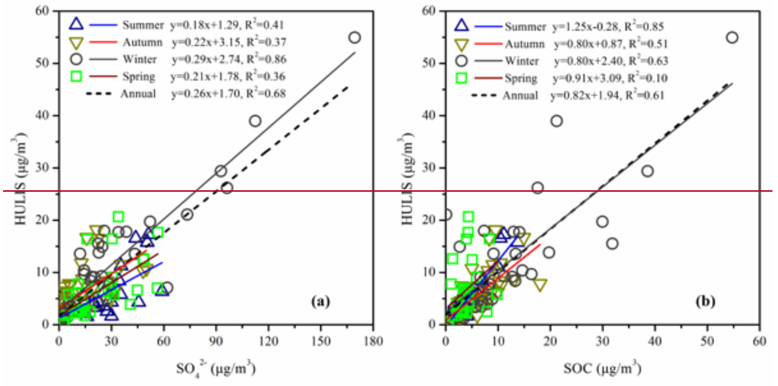


Figure 2. Correlations between HULIS and POC (a), HULIS & EC (b), HULIS & K^+(c), HULIS & Cl^-(d), HULIS & Ca^{2+}(e). Concentrations in four seasons are represented by different shaped points with different colors. Linear regressions are also given with corresponding equations.



~~**Figure 3.** Correlations between HULIS & SO_4^{2-} (a), HULIS and SOC (b). Concentrations in four seasons are represented by different shaped points with different colors. Linear regressions are also given with corresponding equations.~~

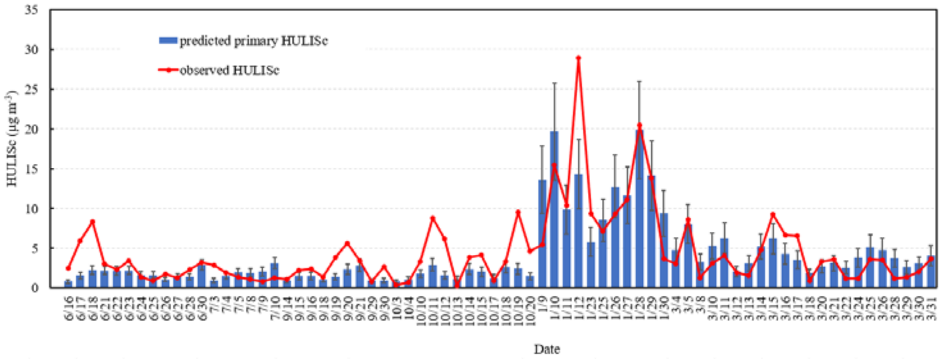


Figure 43. Predicted primary HULISc and observed HULISc concentrations on the days with relatively good primary $PM_{2.5}$ model performance. Error bar is the standard deviation of prediction, which is calculated as described in SI Text S3.1.

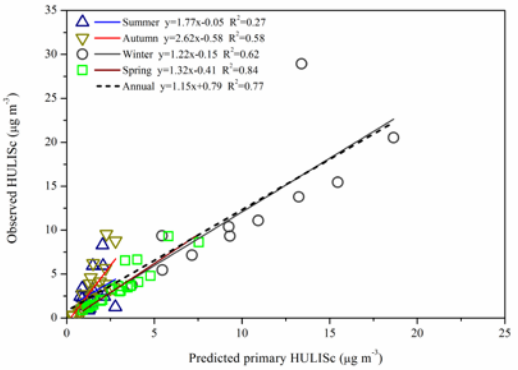


Figure ~~5~~4. Scatter plot of predicted primary HULISc and observed HULISc concentrations. Concentrations of each seasons are represented by different shaped points with different colors. Linear regressions are also given with corresponding equations.

Tables

Table 1. Summary of the concentrations of PM$_{2.5}$, carbon species, water-soluble ions and percentages of several species to some others.

Species	Average	Summer	Autumn	Winter	Spring
	Average ± SD	Average ± SD	Average ± SD	Average ± SD	Average ± SD
PM$_{2.5}$ (μg/m^3)	106±89	98 ± 60	58±48	150±121	120±76
OC (μg/m^3)	16.0±15.8	8.5±5.2	10.3±7.4	28.9±22.0	14.6±10.8
EC (μg/m^3)	5.0±4.8	3.3±1.8	3.5±2.9	7.8±6.6	5.3±4.7
OC/EC	3.6±1.4	2.8±0.8	3.8±1.9	4.3±1.2	3.3±0.9
WSOC (μg/m^3)	6.5±6.5	4.4±3.6	5.2±4.0	10.3±9.8	5.9±4.9
HULIS (μg/m^3)	7.5±7.8	5.5±4.4	5.6±4.7	12.3±11.7	6.5±5.5
HULIS/PM$_{2.5}$ (%)	7.2±3.3	5.9±3.5	9.4±3.1	7.9±2.5	4.8±1.7
HULIS$_C$/OC (%)	24.5±8.3	29.2±6.2	26.2±9.6	21.0±7.1	22.0±6.9
HULIS$_C$/WSOC (%)	59.5±9.2	66.7±5.4	54.1±11.2	62.3±5.7	56.6±6.3
SO$_4^{2-}$ (μg/m^3)	22.3±24.1	22.6±17.0	10.9±13.2	32.7±35.1	22.5±16.5
NO$_3^-$ (μg/m^3)	18.6±18.0	17.2±13.4	10.8±13.2	20.1±17.8	29.0±23.8
Cl$^-$ (μg/m^3)	4.2±4.9	1.8±1.9	1.3±1.6	6.5±5.7	7.9±5.2
Na$^+$ (μg/m^3)	0.60±0.51	0.40±0.30	0.33±0.41	0.89±0.61	0.79±0.36
K$^+$ (μg/m^3)	2.2±2.6	2.2±2.9	1.3±1.0	3.2±3.6	2.2±1.3
Mg^{2+} (μg/m^3)	0.18±0.19	0.15±0.07	0.18±0.08	0.24±0.32	0.10±0.07
Ca^{2+} (μg/m^3)	0.97±0.57	0.99±0.52	1.14±0.48	0.83±0.70	0.89±0.46
NH$_4^+$ (μg/m^3)	14.1±13.0	13.2±9.8	6.6±7.0	19.1±16.9	18.4±11.8

Table 2. HULIS$_C$/OC and HULIS$_C$/WSOC values in the source samples

Source type	Stove/vehicle	HULIS$_C$/OC	HULIS$_C$/WSOC	n
Residential biofuel burning				
wood burning	improve stove	0.41±0.07	0.62±0.06	3
wheat straw	improve stove	0.50±0.04	0.65±0.05	4
corn stover	improve stove	0.42±0.04	0.62±0.04	3
Residential chunk coal combustion				
SM, Var=32.4%	high efficiency heating stove	0.14±0.07	0.51±0.04	3
JY, Var=27.7%	high efficiency heating stove	0.18±0.04	0.50±0.04	3
BH, Var=25.0%	high efficiency heating stove	0.08±0.02	0.44±0.01	3
DT, Var=19.4%	high efficiency heating stove	0.15	0.62	1
SM, Var=32.4%	traditional cooking and heating stove	0.06±0.01	0.46±0.02	3
JY, Var=27.7%	traditional cooking and heating stove	0.07±0.03	0.41±0.06	3
BH, Var=25.0%	traditional cooking and heating stove	0.05±0.01	0.43±0.08	3
Residential briquette coal combustion				
XM, Var=9.6%	high efficiency heating stove	0.24±0.07	0.53±0.09	3
Vehicle exhaust				
traffic tunnel	mixed of gasoline and diesel vehicles	0.05	0.65	1
heavy-duty diesel trucks	Euro II	0.16±0.02	0.38±0.03	3
light-duty gasoline vehicles	Euro IV	0.11±0.03	0.21±0.11	4

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).

Table 3. Average and seasonal contributions percent of various sources to ambient HULIS concentrations in Beijing (%)

	Residential biofuel burning	Residential coal burning	Transportation	Industries	Biomass open burning	Secondary process
Annual	47.1±6.5	15.1±2.9	2.0±0.3	1.3±0.3	1.7±0.5	38.9±9.1
Summer	29.2±6.5	9.4±2.7	3.9±1.1	2.9±1.2	10.3±3.7	50.2±19.3
Autumn	24.8±5.5	8.0±2.3	2.7±0.8	1.7±0.8	1.1±0.6	63.2±18.3
Winter	55.7±14.1	17.9±6.3	1.1±0.4	0.6±0.3	0.0±0.0	30.3±17.2
Spring	62.7±12.8	20.1±5.4	2.0±0.5	1.2±0.4	0.1±0.1	25.4±13.3

	~~Residential biofuel burning~~	~~Residential coal burning~~	~~Transportation~~	~~Industries~~	~~Biomass open burning~~	~~Secondary process~~
~~Average~~	~~57.4±9.1~~	~~12.3±2.8~~	~~1.5±0.3~~	~~1.1±0.3~~	~~1.7±0.5~~	~~25.9±9.3~~
~~Summer~~	~~36.3±8.7~~	~~7.8±2.6~~	~~2.9±0.9~~	~~2.4±1.2~~	~~10.3±3.5~~	~~40.2±18.1~~
~~Autumn~~	~~34.7±8.2~~	~~7.4±2.3~~	~~2.3±0.7~~	~~1.6±0.8~~	~~1.3±0.7~~	~~52.7±17.1~~
~~Winter~~	~~69.6±20.2~~	~~14.9±6.1~~	~~0.8±0.3~~	~~0.5±0.3~~	~~0.0±0.0~~	~~14.3±18.2~~
~~Spring~~	~~69.7±17.0~~	~~14.9±5.1~~	~~1.3±0.4~~	~~0.9±0.4~~	~~0.1±0.0~~	~~13.1±13.4~~

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 of the PPM$_{2.5}$ and f$_{OC}$ values are 30% and 15%, respectively. Uncertainty calculations based on larger uncertainties (50% for both PPM$_{2.5}$ and f$_{OC}$) show 5-10% higher relative uncertainties for the residential biofuel and secondary process but small changes for other primary sectors (see Table S5).

Supplement of

Quantifying primary and secondary humic-like substances in urban aerosol based on emission source characterization and a source-oriented air quality model

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Text S1 Separation and Chemical Analysis of HULIS

A 17.35 cm^2 sample was punched from the high-volume quartz filters and extracted with 8.0 ml of ultra-pure water in an ultrasonic bath for 1 h. It was sonicated for an additional 1 h before allowing the solution to equilibrate at room temperature for 20 h (Chen and Bond, 2010). The extracts were then filtered with 0.22 μm syringe filters to remove debris and insoluble particles. A 3.0 ml portion of the filtered extract was diluted to 15.0 ml for TOC analysis. Another 3.0 ml was acidified to pH=2 using 1 mol L^{-1} HCl and loaded onto the solid phase extraction (SPE) cartridge (Oasis® HLB, 30 μm, 60 mg/cartridge, Waters, USA) that had been activated previously using 3.0 ml of methanol (G.R.) and 6.0 ml ultra-water. Hydrophilic organic compounds with acidic functional groups protonated at pH=2 were retained by the column, while the majority of inorganic species, low-molecular-weight organic acids, and sugars were not retained by the SPE cartridge and appeared in the effluent solution (Lin et al., 2010b; Song et al., 2012). The column was rinsed with 2×0.5 ml of ultra-water to remove the residues of inorganic constituents and then was freeze-dried (Fan et al., 2012). Subsequently, the column retained HULIS was rinsed with 3×0.5 ml of methanol containing 2% ammonia (w/w). The resulting eluate was then evaporated to dryness using a stream of N_2 and re-dissolved in 15.0 mL of ultra-water for TOC analysis of the HULIS.

Before the collected samples were processed, standard Suwannee River Fulvic Acid Standard I (SRFA, International Humic Substances Society) was used to quantify the method recovery. Four different concentrations at 10, 20, 50 and 100 μg/ml of standard solutions were prepared. A portion of each was analyzed by TOC and another was extracted using the SPE column. Three parallel analyses were conducted. During the experimental processes, ultra-pure water served as blanks (*n*=9) and were also loaded onto the SPE column accompanying the isolation method of collected samples. In previous studies, SRFA was often used as standard reference substance to evaluate the analytical performance due to its similarity to atmospheric HULIS (Fan et al., 2012; Stone et al., 2009; Baduel et al., 2009; Lin et al., 2010b; Sullivan and Weber, 2006). Therefore, we also utilized SRFA to quantify the isolation recovery that was defined as the ratio between the carbon content extracted by SPE column and the SRFA aqueous solutions with different concentrations determined by TOC-Vcph.

For both concentrations, recovery was consistent (Correlation coefficient R^2=0.99) but not complete (Figure S3), the average recovery from all of the standard solutions was 89.3 ± 5.3% (*n*=12), slightly lower than several previous studies. Lin et al. (2010b) exhibited a high recovery of 94 ± 2% (*n*=4) using the measuring method of ELSD (evaporative light scattering detector), Fan et al. (2012) also showed similar yields of 94.2-94.4% based on the isolation methods of ENVI-18, XAD-8 and DEAE and determined by TOC, but a relative low yield of 91.4 ± 1.7% (*n*=5) based on SPE was also exhibited. A comparable recovery of ~93% was also displayed both in the studies of Sullivan and Weber (2006) and Badual et al. (2009) based on the isolation methods of XAD-8 and DEAE respectively. The incomplete recovery is probably ascribed to the irreversible reactions between the sorbents and several higher molecular weight organic compounds in solutes (Badual et al., 2009).

The reproducibility was assessed using the relative standard deviation (RSD). As shown in Figure S3, RSD at 10, 20, 50 and 100 μg/ml were 4.7%, 2.3%, 3.4% and 4.2% (*n*=3 for each point), respectively, relatively higher than the results of Fan et al. (2012) and Badual et al. (2009) based on the SPE, ENVI-18 and DEAE methods but lower than the XAD-8 methods (9.5%). The detection limit (DL) of HULIS, defined as three times the standard deviation of the blank plus the average blank, was 7.2 μgC/ml in aqueous solution, comparable with the value (7 μgC/ml) reported by Lin et al. (2010). Analytical uncertainty of the HULIS determination method was estimated to be 10%.

Text S2 Estimation of POC and SOC

POC and SOC was estimated using EC tracer method (Lim and Turpin, 2002; Turpin and Huntzicker, 1995), which has been widely adopted in atmospheric research (Cao et al., 2004; Yu et al., 2004), although it was argued that lack of clear quantitative criteria in selection of data base for $(OC/EC)_{primary}$ determination (Wu and Yu, 2016).

$$SOC = OC - EC \cdot (OC/EC)_{primary} \qquad (S1)$$

$$POC = EC \cdot (OC/EC)_{primary} \qquad (S2)$$

where OC, EC, POC and SOC (secondary organic carbon) are mass concentrations ($\mu g/m^3$). $(OC/EC)_{primary}$ is taken as the minimum of OC/EC in each seasonal samples and its value are 1.45, 1.36, 2.08, 2.21 for summer, autumn, winter and spring, respectively.

Based on the method, the percentages of estimated SOC contributing to OC were comparable with previous results derived from observation by high-resolution time-of-flight aerosol mass spectrometer (AMS) during the same sampling period (Sun et al., 2016; Xu et al., 2017). This indicated that EC tracer method can be used to estimate POC and SOC in our study.

Text S3 Uncertainty estimation for primary and secondary HULISc

S3.1 Uncertainty of daily HULISc

The uncertainty in the calculated daily HULIS*c* using equation (1) for each sector is estimated by assuming that each term on the righthand side of equation (1) are independent random numbers that follow normal distributions. The relative uncertainty (μ) (standard deviation/mean concentration) of the estimated $PPM_{2.5}$ and f_{OC} are 30% and 15%, respectively. The relative uncertainties in the f_{HULISc} for residential coal burning, residential biofuel and transportation sources are 56%, 11% and 52%, based on measurement uncertainty. The uncertainties of f_{HULISc} for dust, power generation and industry sectors are assumed to be 100%, as no measurement data are currently available. The relative uncertainty for open burning is assumed to be 11%, the same value used for residential biofuel. The relative uncertainty for the calculated primary HULIS*c*, is estimated using error propagation equation (S3),

$$\mu_{HULIS_{c,i}} = \sqrt{\mu^2_{PPM2.5} + \mu^2_{f_{OC}} + \mu^2_{f_{HULIS,i}}} \qquad \text{(S3)}$$

Base on the equation, the relative uncertainty for primary HULISc of the residential and transportation sectors are 35.3% (residential biofuel), 65.3% (residential coal) and 61.9% (transportation), respectively. For dust, power, and industrial sectors, the relative uncertainty is estimated to be 105.5%. Open burning is assumed to have the same uncertainty (35.3%) as the residential biofuel sector. The absolute uncertainty (standard deviation σ) for total primary HULISc ($HULIS_c^p$) is calculated based on equation (S4):

$$\sigma_{HULIS_c^p} = \sqrt{\sum_{i=1}^{N} \sigma^2_{HULISc,i}} \qquad \text{(S4)}$$

where N is the number of primary HULIS*c* sectors. The absolute uncertainty σ for each sector is determined by multiplying the concentration of HULISc of that sector with the relative uncertainty from equation (S3). The observed daily total HULISc is assumed to have a relative uncertainty of 10%. The absolute uncertainty of calculated daily secondary HULISc concentration is estimated using an error propagation equation similar to equation (S4). When a predicted total daily primary HULISc is higher than observed total concentrations, the total primary HULISc concentration is set to equal the observed total concentrations with a relative uncertainty of 100%, and the secondary HULISc concentration is set to zero.

S3.2 Uncertainty of seasonal and annual HULISc

Uncertainty of seasonal average HULISc concentrations for each primary sector, the secondary process and the total HULISc are estimated using a bootstrap technique. In summary, for each season with N days of valid daily data, a new set of data with N daily data was prepared by randomly picking data from the original dataset. The same data can be picked multiple times and thus can be repeated in the new dataset. Average HULISc concentrations for the primary sectors, secondary process and total concentrations are calculated for the new dataset. This process is repeated M times (M is a large number). To account for the uncertainty in the daily average concentrations, the daily concentrations are randomly modified using a normal distribution function for each bootstrap run. Finally, the mean and standard deviation of the average concentrations from each bootstrap run are calculated and reported as the seasonal average concentrations and their uncertainties. Uncertainties in the relative contributions reported in Table S3 are then calculated using an error propagation equation similar to equation (S3). Uncertainty in the annual average concentrations and contributions are determined using seasonally stratified bootstrap sampling. Two different set of bootstrap runs with M=10,000 and 50,000. No significant differences were noticed. The results reported in Table 3 are based on the run with M=10,000.

Tables

Table S1. Summary of atmospheric HULIS contents reported in previous literatures.

Location	Period	Sample tyoe	HULIS (μg/m^3)	HULIS$_C$/ WSOC (%)	HULIS/HULIS$_C$	Reference
Jungfraujoch, Switzerland, high-alpine	Jul. – Aug. 1998, Summer.	PM2.5	~0.7	54	1.9	Krivácsy et al., 2001
K-puszta, Hungary, rural	Jan. 5 - Apr. 11, 2000, Colder season;	PM1.5	4.4	57 (38-72)	1.93	Kiss et al., 2002
	Apr. 12 - Sep. 14, 2000, Heater season.		3.4			
Near Aveiro, Portugal, rural-coastal	Jul. 2002 – Jul. 2003.	PM2.5	~1.8	~52	1.71-1.95	Duarte et al., 2007
Budapest, Hungary, urban	Apr. 23 - May 5, 2002.	PM2.5	2.0	62	1.81	Salma et al., 2007
Auckland, New Zealand, marine	Jan. and Feb., 2001, Summer;	PM10	~0.66	51		Krivácsy et al., 2008
urban;	Jun. and Jul., 2001, Winter.	PM10	~4.01	47		
	Jan. and Feb., 2001, Summer;	PM10	~0.46	34		
Christchurch, New Zealand, marine	Jun. and Jul., 2001, Winter.	PM10	~10.34	45		
urban;	Apr. – May 2002.	PM2.5	~1.71	25		
Budapest, Hungary, urban;	Aug. 13 – Sep. 5, 2001.	PM1.5	~0.76	19		
Mace Head, Ireland, marine, pristine background						
Budapest, Hungary, urban	May 2-9, 2006, Spring;	PM2.5	4.7	47	1.81	Salma et al., 2008
	Jul. 17-24, 2006, Summer.		3.8			
4 cities, France, urban;	Nov. 2007 – Feb. 2008, Winter.	PM10	~2.13	~38		Badual et al., 2010
3 cities, France, urban;	May. – Aug., 2008, Summer;		~0.59	~36		
Grenoble, France, urban;	Sep. – Oct. and Mar. – Apr. 2008, Mid-season;		~0.76	~29		
Chamonix, France, rural (Biomass burning background).	Dec. 2007, Winter.		1.47	~23.4		
South China, rural	Nov. 15-22, 2007.	PM2.5	11.8 ± 5.8	60±11	1.94	Lin et al., 2010b
K-puszta, Hungary, rural;	May 4 and May 6, 2008;	PM2.5	1.65	35	1.93	Salma et al., 2010
Budapest, Hungary, urban;	Jun. 3-10, 2008;		2.2	48	1.81	
Amazon Rainforest, Rondônia, Brazil, (Biomass burning background)	Sep. 18-22, 2002 (Daylight & Night).		43 & 60	63 & 76	2.04	
Melpitz, Germany, rural;	Jan. 1 – Feb. 25, 2009	PM2.5	2.2	49		Kristensen et al., 2012
Northwestern Colorado, USA, urban	Aug. 7 – Sep. 2, 2010		0.46	53		
Seoul, Korea, urban	Dec. 27, 2010 – Jan. 20, 2011		6.46	60		Park et al., 2012
New York, the USA, rural	Jul. – Aug. 2009, Summer	PM2.5				Pavlovic & Hopke,
	Daylight (250nm & 280nm);		0.84 &	39 & 25		2012
	Night (250nm & 280nm).		0.54	47 & 30		
	Sep. – Oct. 2009, Fall (250nm & 280nm).		1.14&0.72	55 & 37		
			1.33 &			
			0.90			
Maofengshan, suburban;	Jul., 2006, Summer. & Jan., 2007, Winter.	TSP	5.7 & 3.3	40.5 &	2.08	Song et al., 2012
University Town, suburban;			4.3 & 7.8	39.4	2.04	
Wushan, urban;			5.8 & 13.4	37 & 44	1.97	
Guangzhou, China				36 & 40.6		
Guangzhou, China, urban	Aug. 16 – Sep. 15, 2011	PM2.5	/	~57	1.86-2.22	Fan et al., 2013
Guangzhou, China, urban;	2009	PM2.5	4.8±3.4	48±13	1.9	Kuang et al., 2015
Nansha, China, suburban			4.7±3.6	57±16		
Shanghai, China, urban	Mar. – May 2013, Spring;	PM1.0	3.08	~42		Qiao et al., 2015
	Jun. – Aug. 2013, Summer;		3.48	~41		
	Sep. – Nov. Autumn;		2.98	~32		

	Dec. 2013 – Feb. 2014, Winter;		6.67	~38	
	Annual.		~4.18	~38	
Shanghai, China, Urban	Dec. 2011 – Feb. 2012, Winter;	PM2.5	6.40	67.3±10.8	Zhao et al., 2015
	Mar. – May 2012, Spring;		5.51	60.3±14.6	
	Jun. – Aug. 2012, Summer;		3.36	59.5±11.6	
	Sep. – Nov. 2012, Autumn.		5.36	64.7±9.1	
Lanzhou, China, Urban	Annual	PM2.5	4.70	0.45±0.06	Tan et al., 2016
	Winter		7.24	0.47±0.05	
	Summer		2.15	0.44±0.06	
Central and southern Europe, Urban	Winter	PM10	1.29~2.8	0.32~0.43	Voliotis et al., 2017
Suixi, China	Summer	PM2.5	2.56		Wang et al., 2017

Table S2. Fuels proximate and ultimate analysis

	Coal					Biofuel		
	SM	JY	BH	DT	XM	wheat straw	maize stover	wood
Proximate analysis (as received, mass %)								
moisture	5.1	8.1	7.2	1.6	2.8	9.8	8.0	9.3
volatile matter	32.4	27.7	25.0	19.4	9.5	65.2	66.8	73.8
fixed carbon	60.1	61.1	59.8	68.0	72.5	17.7	20.7	15.9
ash	2.4	3.2	7.9	11.0	15.1	7.3	4.5	1.0
Ultimate analysis[a] (dry basis, mass %)								
C	77.5	73.1	72.6	74.5	79.9	41.1	43.9	47.0
H	4.6	4.6	4.5	3.6	1.5	5.1	6.1	5.8
N	0.99	0.90	0.71	0.54	0.66	0.64	0.75	0.14
S	0.21	0.19	0.30	0.42	0.38	0.06	0.12	0.10

[a] Analysis by CHNS elemental analyzer (Vario EL, Elementar, Langenselbold, Germany)

Table S3. Summary of HULISc/OC and HULIS/WSOC values from biomass 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 (M=7~14.8%)	Chimney type logwood stove with primary/secondary air	Dilution source sampler with DR=10, RT long enough (no specified)	0.04-0.11		Goncalves et al., 2010
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.

Table ~~S3~~S4. Values of f_{OC} used in this study ~~(Ying et al., 2018)~~.

Source	f_{OC}	data source ~~(SPECIATE database profile #)~~
Dust	0.69%	413502.5[a]
Residential coal combustion	62.80%	91028[a]
Residential biofuel burning	42.51%	Li et al., 2009
Transportation	51.17%	90% 91022 + 10% 3914[a]
Power	2.63%	91104[a]
Industry	8.00%	900162.5[a]
open burning	29.40%	average of 92000, 92090[a]~~, 92084~~

Note: US EPA SPECIATE database profile #

Table ~~S4~~S5. Annual and seasonal contributions percent of anthropogenic various primary emission of HULIS in Beijing (%)

Source types	Annual	Spring	Summer	Autumn	Winter
Power plants	0.0	0.0	0.0	0.0	0.0
Industries	2.9	4.8	6.2	3.3	1.4
Residential coal burning	24.6	23.8	23.2	24.4	25.2
Residential biofuel burning	70.8	68.6	66.9	70.3	72.5
Transportation	1.7	2.8	3.7	2.0	0.8

Table ~~S5~~S6. Average and seasonal contributions percent of various sources to ambient HULIS concentrations in Beijing (%) using relative uncertainties of 50% for both $PPM_{2.5}$ and f_{OC}.

	Residential biofuel burning	Residential coal burning	Transportation	Industries	Biomass open burning	Secondary process
Annual	46.9±9.5	15.1±3.7	2±0.4	1.3±0.3	1.7±0.6	39.1±12
Summer	29.1±9	9.4±3.4	3.9±1.4	2.9±1.4	10.3±4.7	50.3±20.6
Autumn	24.7±7.4	7.9±2.8	2.7±1	1.7±0.9	1.1±0.7	63.2±19.3
Winter	55.7±20.8	17.9±8.1	1.1±0.5	0.6±0.3	0±0	30.6±24.1
Spring	62.2±17.7	20.1±6.7	2±0.6	1.2±0.5	0.1±0.1	25.5±18.5

	~~Residential biofuel burning~~	~~Residential coal burning~~	~~Transportation~~	~~Industries~~	~~Biomass open burning~~	~~Secondary process~~
~~Average~~	~~57.4 ± 14.1~~	~~12.3 ± 3.7~~	~~1.5 ± 0.3~~	~~1.1 ± 0.3~~	~~1.7 ± 0.7~~	~~25.9 ± 14.4~~
~~Summer~~	~~36.3 ± 12.7~~	~~7.8 ± 3.3~~	~~2.9 ± 1.2~~	~~2.4 ± 1.3~~	~~10.3 ± 4.9~~	~~40.2 ± 21.0~~
~~Autumn~~	~~34.7 ± 11.1~~	~~7.4 ± 2.8~~	~~2.3 ± 0.9~~	~~1.6 ± 0.9~~	~~1.3 ± 0.8~~	~~52.7 ± 18.9~~
~~Winter~~	~~69.6 ± 30.7~~	~~14.9 ± 8.0~~	~~0.8 ± 0.4~~	~~0.5 ± 0.3~~	~~0.0 ± 0.0~~	~~14.3 ± 29.8~~
~~Spring~~	~~69.7 ± 25.4~~	~~14.9 ± 6.4~~	~~1.3 ± 0.6~~	~~0.9 ± 0.5~~	~~0.1 ± 0.1~~	~~13.1 ± 23.4~~

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 $PPM_{2.5}$ and f_{OC} values are 50%. Uncertainty calculations based on less uncertainties (30% for $PPM_{2.5}$ and 15% for f_{OC}) are shown in Table 3 in main text.

Figures

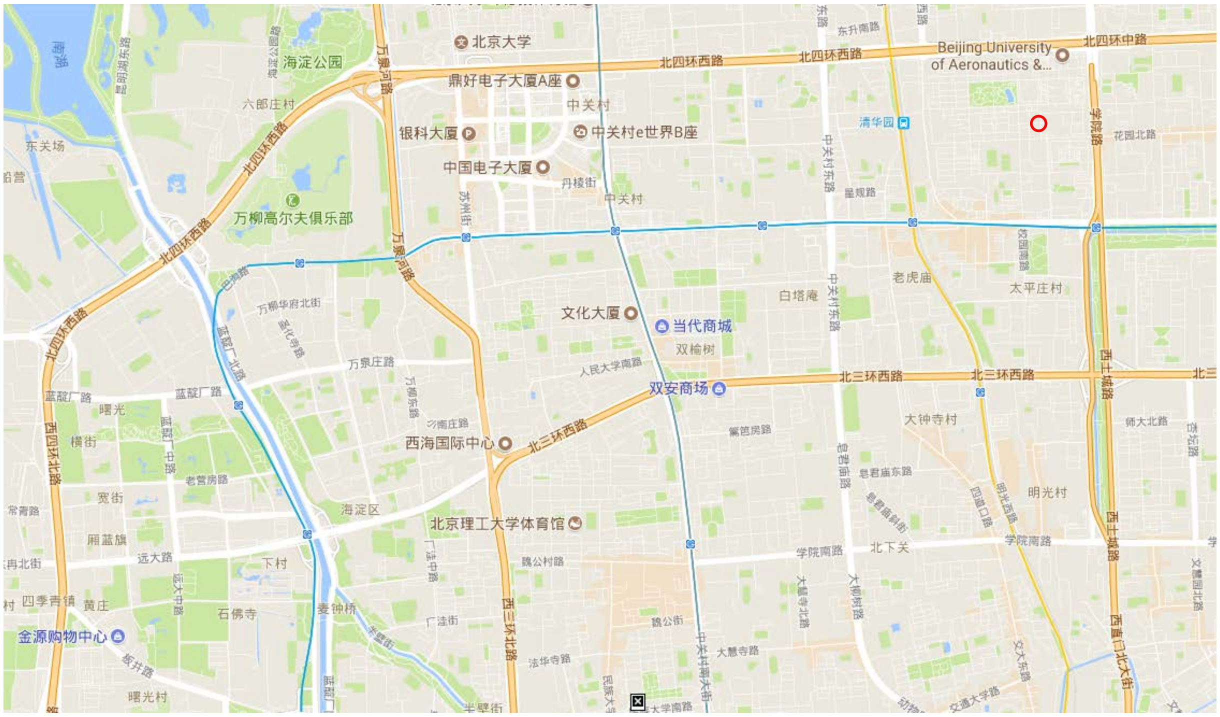

Figure S1. Location of the sampling sites (Highlighted with a red circle)

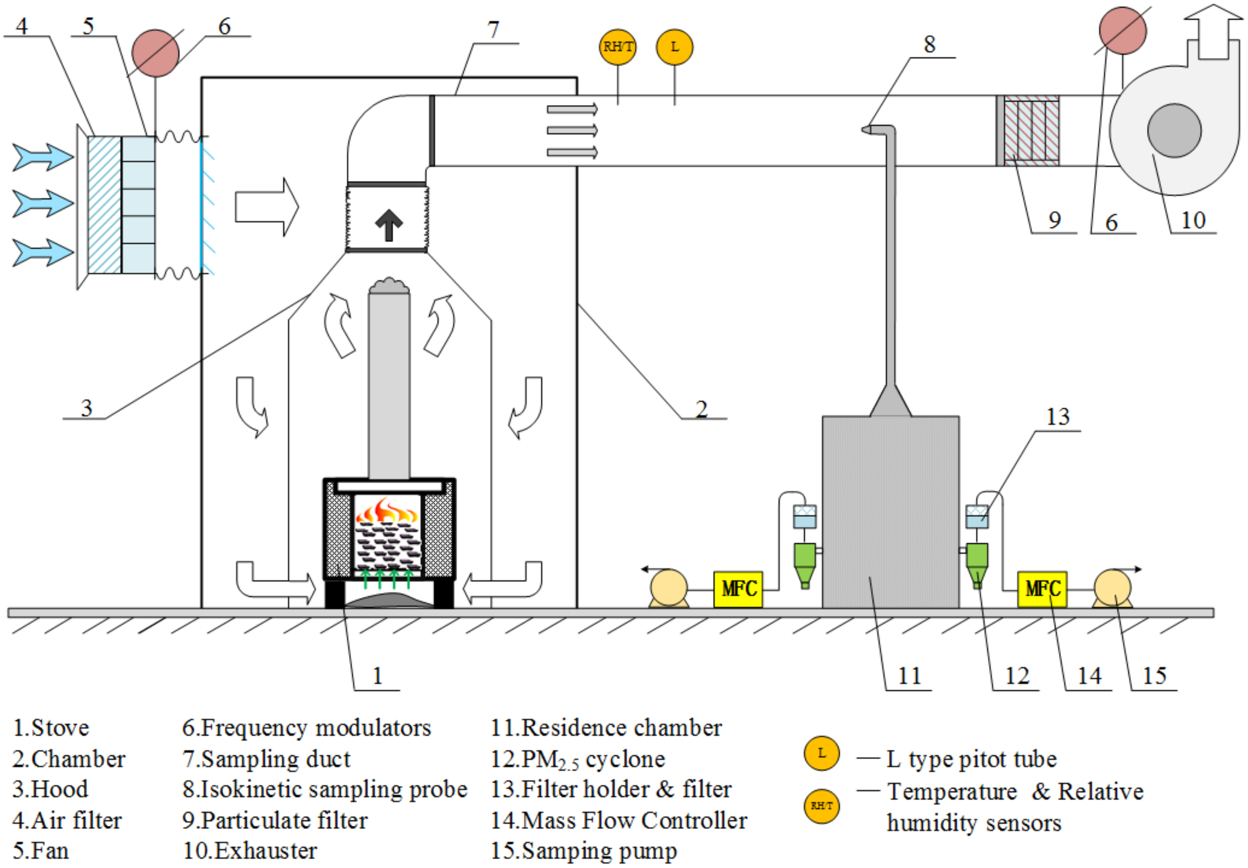

Figure S2. An outline of the sampling system for source testing of residential biofuel and coal combustion.

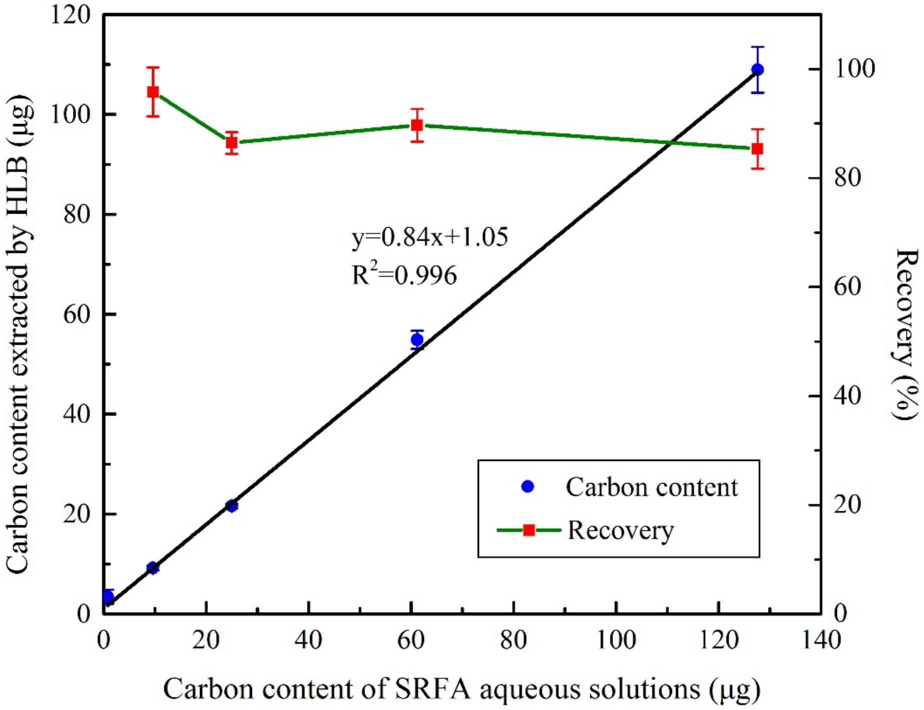

Figure S3. Recovery of HULIS from the SRFA standard solutions using SPE cartridges

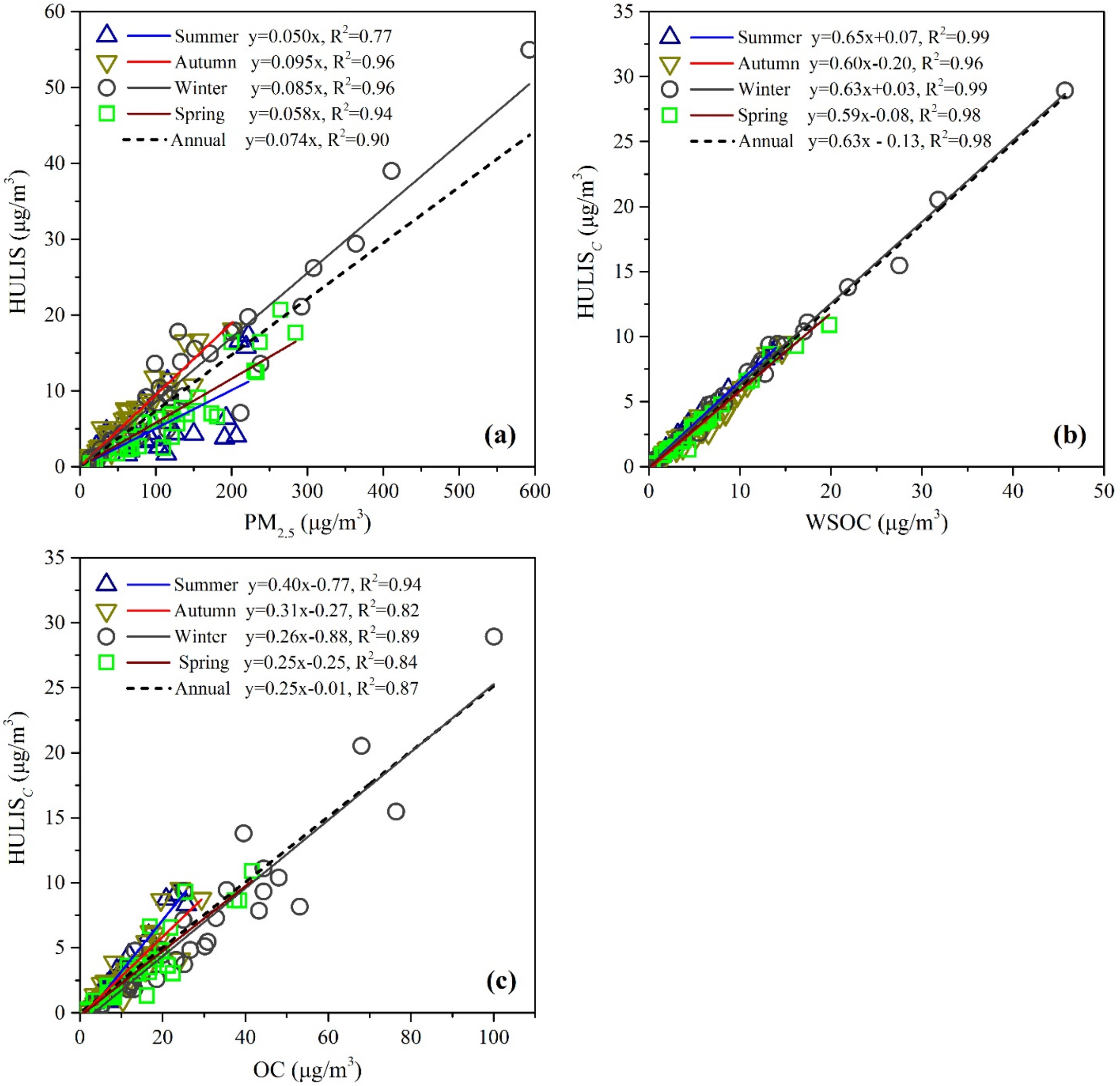

Figure S4. Correlations of (a) seasonal HULIS & $PM_{2.5}$ (b) seasonal $HULIS_C$ & WSOC and (c) seasonal $HULIS_C$ & OC.

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