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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

Text S1. Separation and Chemical Analysis of HULIS

A 17.35 cm² 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 N₂ 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 $89.3 \pm 5.3\%$ (*n*=12), slightly lower than several previous studies. Lin et al. (2010b) exhibited a high recovery of $94 \pm 2\%$ (*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 $91.4 \pm 1.7\%$ (*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 $\mu\text{gC/ml}$ in aqueous solution, comparable with the value (7 $\mu\text{gC/ml}$) 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 were estimated using the 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). However, it has been argued that there is a lack of clear quantitative criteria in the selection of basis for determining $(OC/EC)_{\text{primary}}$ (Wu and Yu, 2016).

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

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

where OC, EC, POC and SOC (secondary organic carbon) are mass concentrations ($\mu\text{g}/\text{m}^3$). $(OC/EC)_{\text{primary}}$ is taken as the minimum of OC/EC in each seasonal samples and its value are 1.45, 1.36, 2.08, and 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 result 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 HULISc using equation (1) for each sector is estimated by assuming that each term on the right hand 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 HULISc, is estimated using error propagation equation (S3),

$$\mu_{HULISc,i} = \sqrt{\mu_{PPM_{2.5}}^2 + \mu_{f_{OC}}^2 + \mu_{f_{HULISc,i}}^2} \quad (S3)$$

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 ($HULISc^p$) is calculated based on equation (S4):

$$\sigma_{HULISc^p} = \sqrt{\sum_{i=1}^N \sigma_{HULISc,i}^2} \quad (S4)$$

where N is the number of primary HULISc 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 $M=10,000$.

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

Location	Period	Sample type	HULIS ($\mu\text{g}/\text{m}^3$)	HULIS _c /WSOC (%)	HULIS/HU LIS _c	Reference
Jungfrauoch, Switzerland, high-alpine	Jul. – Aug. 1998, Summer.	PM _{2.5}	~0.7	54	1.9	Krivácsy et al., 2001
K-pusztá, Hungary, rural	Jan. 5 - Apr. 11, 2000, Colder season; Apr. 12 - Sep. 14, 2000, Heater season.	PM _{1.5}	4.4 3.4	57 (38-72)	1.93	Kiss et al., 2002
Near Aveiro, Portugal, rural-coastal	Jul. 2002 – Jul. 2003.	PM _{2.5}	~1.8	~52	1.71-1.95	Duarte et al., 2007
Budapest, Hungary, urban	Apr. 23 - May 5, 2002.	PM _{2.5}	2.0	62	1.81	Salma et al., 2007
Auckland, New Zealand, marine urban;	Jan. and Feb., 2001, Summer;	PM ₁₀	~0.66	51		
Christchurch, New Zealand, marine urban;	Jun. and Jul., 2001, Winter.	PM ₁₀	~4.01	47		
Budapest, Hungary, urban;	Jan. and Feb., 2001, Summer;	PM ₁₀	~0.46	34		Krivácsy et al., 2008
Mace Head, Ireland, marine, pristine background	Jun. and Jul., 2001, Winter. Apr. – May 2002.	PM ₁₀ PM _{2.5}	~10.34 ~1.71	45 25		
Budapest, Hungary, urban	Aug. 13 – Sep. 5, 2001. May 2-9, 2006, Spring; Jul. 17-24, 2006, Summer.	PM _{1.5} PM _{2.5}	~0.76 4.7 3.8	19 47	1.81	Salma et al., 2008
4 cities, France, urban; 3 cities, France, urban; Grenoble, France, urban; Chamonix, France, rural (Biomass burning background).	Nov. 2007 – Feb. 2008, Winter. May. – Aug., 2008, Summer; Sep. – Oct. and Mar. – Apr. 2008, Mid-season; Dec. 2007, Winter.	PM ₁₀	~2.13 ~0.59 ~0.76 1.47	~38 ~36 ~29 ~23.4		Badual et al., 2010
South China, rural	Nov. 15-22, 2007.	PM _{2.5}	11.8 ± 5.8	60±11	1.94	Lin et al., 2010b
K-pusztá, Hungary, rural; Budapest, Hungary, urban; Amazon Rainforest, Rondônia, Brazil, (Biomass burning background)	May 4 and May 6, 2008; Jun. 3-10, 2008; Sep. 18-22, 2002 (Daylight & Night).	PM _{2.5}	1.65 2.2 43 & 60	35 48 63 & 76	1.93 1.81 2.04	Salma et al., 2010
Melpitz, Germany, rural; Northwestern Colorado, USA, urban	Jan. 1 – Feb. 25, 2009 Aug. 7 – Sep. 2, 2010	PM _{2.5}	2.2 0.46	49 53		Kristensen et al., 2012
Seoul, Korea, urban	Dec. 27, 2010 – Jan. 20, 2011 Jul. – Aug. 2009, Summer Daylight (250nm & 280nm);	PM _{2.5}	6.46 0.84 & 0.54	60 39 & 25		Park et al., 2012
Potsdam, New York, the USA, rural	Night (250nm & 280nm). Sep. – Oct. 2009, Fall (250nm & 280nm)	PM _{2.5}	1.14 & 0.72 1.33 & 0.90	47 & 30 55 & 37		Pavlovic & Hopke, 2012
Maofengshan, suburban; University Town, suburban; Wushan, urban; Guangzhou, China	Jul., 2006, Summer. & Jan., 2007, Winter.	TSP	5.7 & 3.3 4.3 & 7.8 5.8 & 13.4	40.5 & 39.4 37 & 44 36 & 40.6	2.08 2.04 1.97	Song et al., 2012
Guangzhou, China, urban	Aug. 16 – Sep. 15, 2011	PM _{2.5}	/	~57	1.86-2.22	Fan et al., 2013
Guangzhou, China, urban; Nansha, China, suburban	2009	PM _{2.5}	4.8±3.4 4.7±3.6	48±13 57±16	1.9	Kuang et al., 2015
Shanghai, China, urban	Mar. – May 2013, Spring; Jun. – Aug. 2013, Summer; Sep. – Nov. Autumn; Dec. 2013 – Feb. 2014, Winter; Annual.	PM _{1.0}	3.08 3.48 2.98 6.67 ~4.18	~42 ~41 ~32 ~38 ~38		Qiao et al., 2015
Shanghai, China, Urban	Dec. 2011 – Feb. 2012, Winter; Mar. – May 2012, Spring; Jun. – Aug. 2012, Summer; Sep. – Nov. 2012, Autumn. Annual	PM _{2.5}	6.40 5.51 3.36 5.36 4.70	67.3±10.8 60.3±14.6 59.5±11.6 64.7±9.1 0.45±0.06		Zhao et al., 2015
Lanzhou, China, Urban	Winter Summer	PM _{2.5}	7.24 2.15	0.47±0.05 0.44±0.06		Tan et al., 2016
Central and southern Europe, Urban	Winter	PM ₁₀	1.29~2.8	0.32~0.43		Voliotis et al., 2017
Suixi, China	Summer	PM _{2.5}	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 HULIS_c/OC and HULIS_c/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 S4. Values of f_{OC} used in this study.

Source	f_{OC}	data source
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

Note: US EPA SPECIATE database profile #

Table 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 S6. Average and seasonal contributions percent of various sources to ambient HULIS concentrations in Beijing (%) using relative uncertainties of 50% for both $\text{PPM}_{2.5}$ 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

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.

Figures

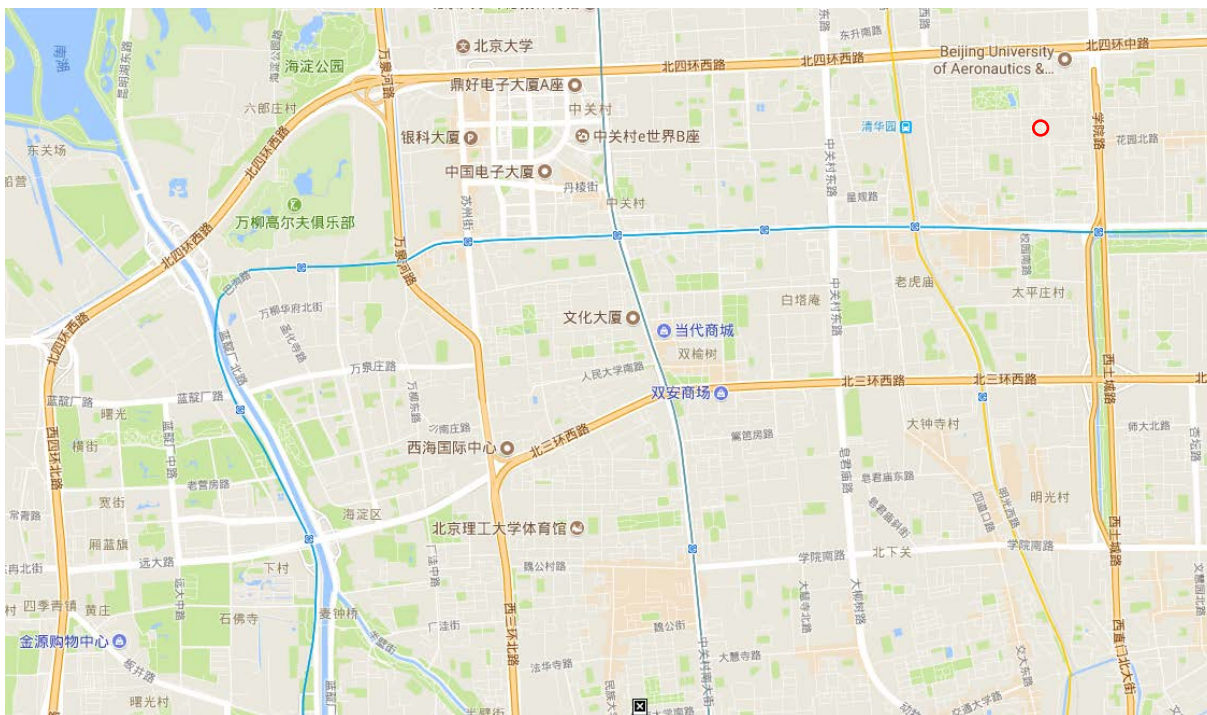


Figure S1. Location of the sampling sites (Highlighted with a red circle)

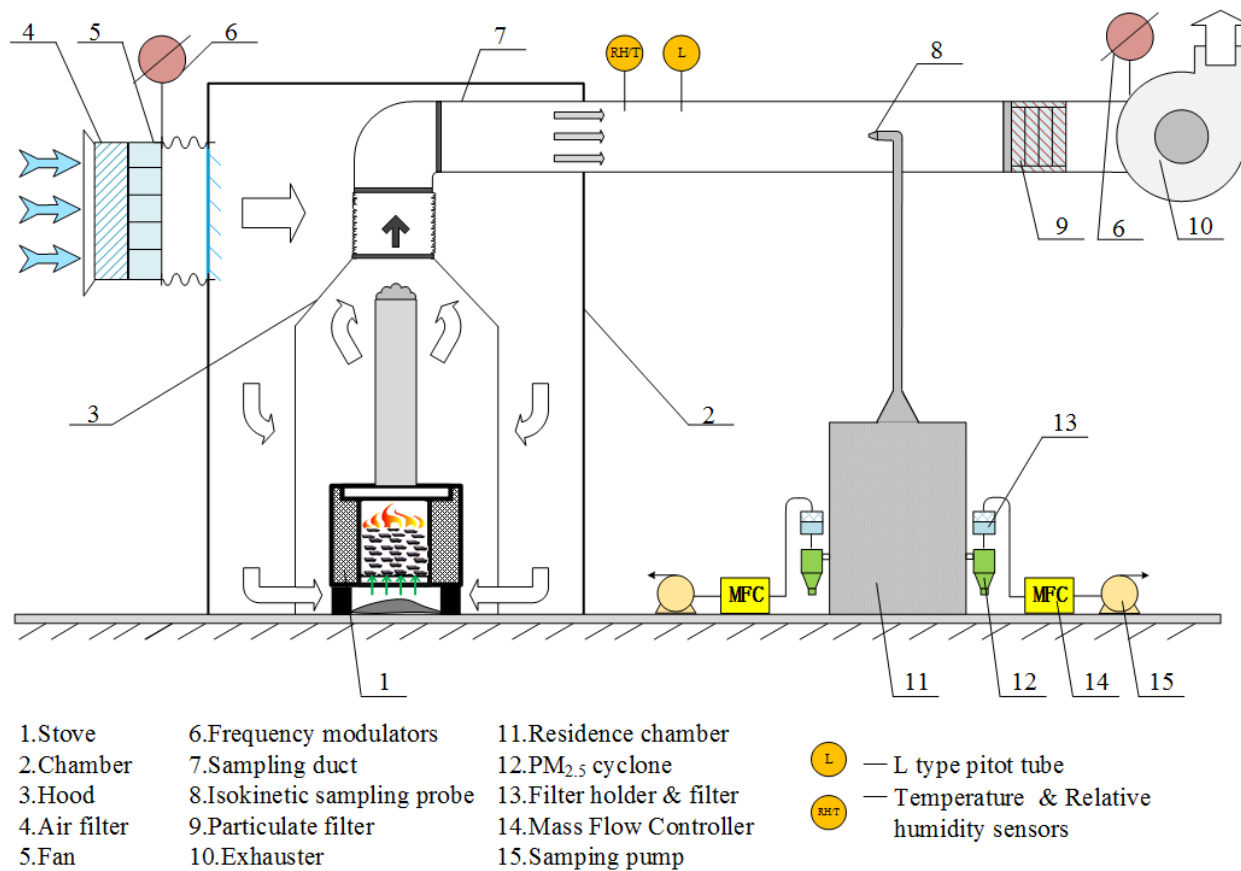


Figure S2. An outline of the sampling system for source testing of residential biofuel and coal combustion.

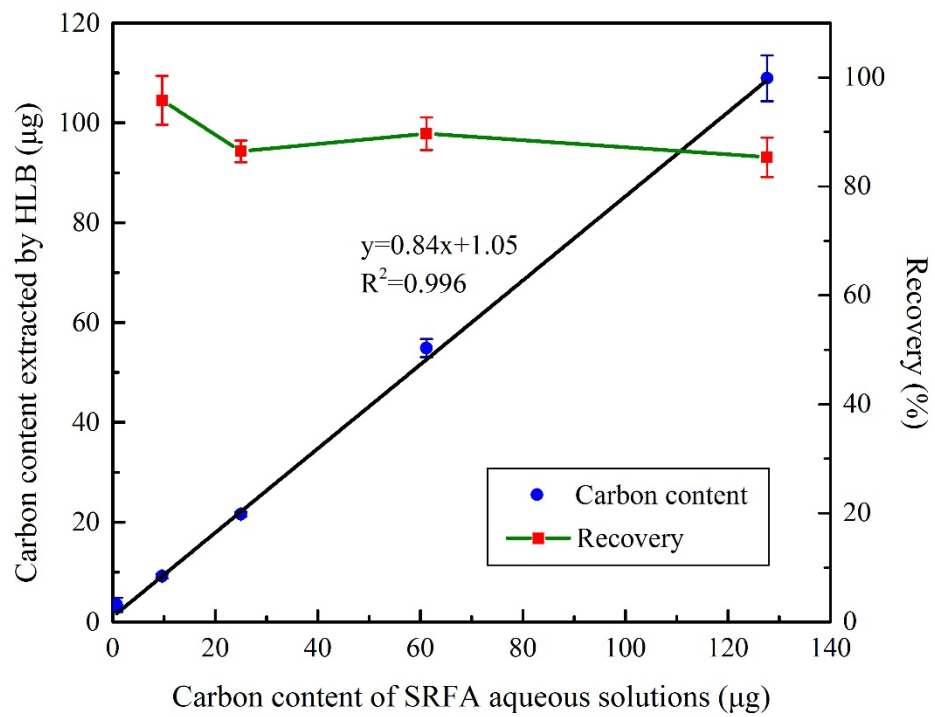


Figure S3. Recovery of HULIS from the SRFA standard solutions using SPE cartridges

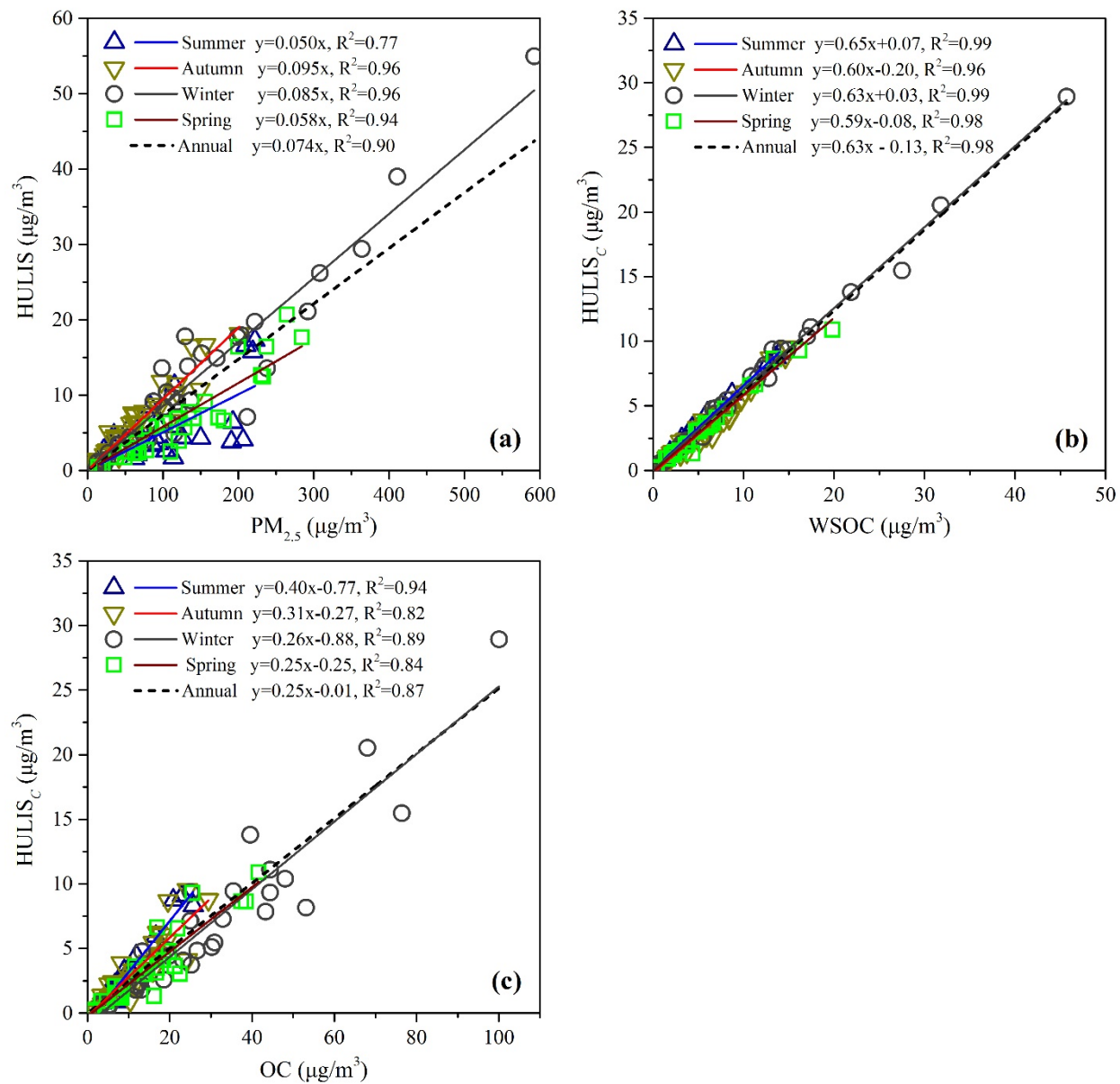


Figure S4. Correlations of (a) seasonal HULIS & $\text{PM}_{2.5}$ (b) seasonal HULIS_C & WSOC and (c) seasonal HULIS_C & OC.

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