

**Sources of Humic-Like Substances (HULIS) in PM<sub>2.5</sub> in Beijing: Receptor Modeling**

**Approach**

Xinghua Li,<sup>1</sup> Kaiqiang Yang,<sup>1</sup> Junzan Han,<sup>1</sup> Qi Ying,<sup>2</sup> Philip K. Hopke<sup>3,4</sup>

<sup>1</sup>School of Space and Environment, Beihang University, Beijing, 100191, China

<sup>2</sup>Zachry Department of Civil Engineering, Texas A&M University, College Station, TX 77843, USA

<sup>3</sup>Center for Air Resources Engineering and Science, Clarkson University, Potsdam, NY 13699 USA.

<sup>4</sup>Department of Public Health Sciences, University of Rochester School of Medicine and Dentistry, Rochester, NY 14642 USA

Correspondence to: phopke@clarkson.edu

**S1. Separation and Chemical Analysis**

A 17.35 cm<sup>2</sup> 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<sup>-1</sup> HCl and loaded onto the solid phase extraction (SPE) cartridge (Oasis<sup>®</sup> 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., 2010; 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<sub>2</sub> 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., 2010; 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 (Fig. 1), 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. (2010) 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 Baduel 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 (Baduel et al., 2009). Incomplete elution may also lead to lower yield (Fan et al., 2012).

The reproducibility was assessed using the relative standard deviation (RSD). As shown in Fig. S1, 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%). Thus, the reproducibility by the SPE isolation and TOC analysis allows the measurements of low concentrations of atmospheric HULIS.

The detection limit (DL) of HULIS was calculated as the sum of the average blank value plus three times the standard deviation of the blank. In this study, the average blank value that had passed through SPE column was about 0.59 µgC/ml ( $n=9$ ), and the corresponding DL value was calculated as about 1.09 µgC/ml. The average value was relatively higher than the average

(~0.28  $\mu\text{gC/ml}$ ,  $\text{SD}=0.05\mu\text{gC/ml}$ ,  $n=18$ ) of ultra-pure water blanks which were determined directly using TOC-Vcph. These results are comparable to the low values of Fan et al. (2012). This difference is probably caused by the effect of methanol, systematic errors or some other unknown factors. Nevertheless, these interferences are relatively small compared to the collected sample masses, and the low DL value suggests that the method is excellent for detecting the low HULIS content in collected aerosol samples.

Table S1. Distributional properties of the species measured in the collected PM<sub>2.5</sub> samples and associated pollutant gases (µg/m<sup>3</sup>).

Species	Minimum	25th Percentile	Median	Mean	75th Percentile	95th Percentile	Maximum
PM <sub>2.5</sub>	4.25	38.10	88.07	107.17	140.01	267.32	592.40
Al	0.03	0.19	0.28	0.35	0.39	0.79	2.22
As	0.00	0.00	0.01	0.02	0.04	0.08	0.28
Br	0.00	0.01	0.02	0.03	0.04	0.08	0.17
Ca	0.01	0.22	0.37	-8.02	0.52	1.06	1.89
Cl-	0.07	0.53	2.47	4.73	7.34	16.20	23.97
Co	0.00	0.00	0.00	0.00	0.00	0.01	0.02
Cu	0.00	0.02	0.03	0.04	0.05	0.10	0.30
EC	0.12	1.82	3.42	5.09	6.89	16.82	22.52
EC1-OP	0.09	1.76	3.18	4.92	6.71	16.32	22.24
EC2	0.12	0.12	0.12	0.21	0.28	0.55	1.02
EC3	0.12	0.12	0.12	0.12	0.12	0.12	0.12
Fe	0.08	0.39	0.66	0.82	1.14	1.87	4.06
HULIS_C	0.50	1.26	3.00	4.11	5.37	10.46	28.92
K+	0.02	0.88	1.70	2.52	3.27	6.65	17.56
Mg	0.03	0.12	0.16	0.21	0.22	0.41	2.39
Mn	0.01	0.03	0.06	0.07	0.09	0.15	0.26
Na+	0.02	0.22	0.57	0.64	1.01	1.67	2.52
NH4+	0.01	4.13	11.39	14.77	21.38	37.96	79.71
Ni	0.00	0.00	0.00	0.00	0.00	0.01	0.01
NO3-	0.11	3.24	13.47	19.35	31.77	64.85	79.70
OC	0.90	6.29	12.29	16.53	21.72	44.37	100.04
OC1	0.12	0.12	0.47	1.66	1.19	8.02	16.12
OC2	0.12	1.73	3.33	3.68	5.06	8.53	15.60
OC3	0.32	1.85	3.19	4.56	6.20	11.76	19.03
OC4	0.12	1.25	2.88	3.87	5.74	10.43	16.67
OPC	0.12	0.33	1.46	2.79	2.70	7.73	44.60

Pb	0.01	0.07	0.20	0.28	0.41	0.72	1.82
Se	0.00	0.00	0.00	0.01	0.00	0.01	0.02
Si	0.08	0.30	0.45	0.55	0.67	1.33	1.98
SO <sub>4</sub> <sup>2-</sup>	0.21	3.97	15.96	22.47	30.34	59.45	169.50
Ti	0.00	0.02	0.03	0.03	0.04	0.07	0.12
V	0.00	0.00	0.00	0.00	0.00	0.01	0.01
WIC	0.21	3.62	6.59	9.73	11.86	29.76	54.34
WSOC	0.21	0.96	2.10	2.69	3.90	6.68	16.77
Zn	0.02	0.14	0.36	0.45	0.62	1.20	2.57
O <sub>3</sub> (ppb)	1.8	17.2	27.8	36.0	43.3	99.8	388.7
NO (ppb)	2.3	15.8	30.4	49.3	69.9	164.4	216.0
NO <sub>2</sub> (ppb)	14.0	50.8	69.4	72.3	90.0	121.5	143.0
SO <sub>2</sub> (ppb)	3.6	12.1	23.9	39.0	58.0	104.0	214.4
CO (ppm)	0.3	0.8	1.4	1.8	2.3	5.4	7.8

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Table S2. Average mass contribution ( $\mu\text{g}/\text{m}^3$ ) to specific species from the sources resolved by PMF from the data set with gases using the constrained								
HULIS	Biomass	Coal	Sulfate	Incinerator	Traffic	Nitrate/Sulfat	Residential	Road
Overall	0.24	0.00	1.09	0.00	0.41	0.03	2.85	0.00
Summer	0.53	0.00	1.47	0.00	0.01	0.00	3.87	0.00
Autumn	0.08	0.00	0.42	0.00	0.15	0.01	1.06	0.00
Winter	0.27	0.00	2.14	0.00	1.09	0.08	2.72	0.00
Spring	0.25	0.00	0.72	0.00	0.32	0.02	4.45	0.00
WSOC	Biomass	Coal	Sulfate	Incinerator	Traffic	Nitrate/Sulfat	Residential	Road
Overall	0.12	0.00	0.48	0.00	0.25	0.09	1.70	0.42
Summer	0.26	0.00	0.65	0.00	0.01	0.00	2.31	0.34
Autumn	0.04	0.00	0.18	0.00	0.09	0.03	0.63	0.42
Winter	0.13	0.00	0.95	0.00	0.67	0.23	1.62	0.43
Spring	0.13	0.00	0.32	0.00	0.19	0.07	2.65	0.45
Sulfate	Biomass	Coal	Sulfate	Incinerator	Traffic	Nitrate/Sulfat	Residential	Road
Overall	2.83	0.00	10.25	0.00	0.71	2.85	1.41	1.04
Summer	6.16	0.00	13.86	0.00	0.02	0.09	1.92	0.84
Autumn	0.96	0.00	3.92	0.00	0.25	1.01	0.53	1.05
Winter	3.11	0.00	20.18	0.00	1.90	7.58	1.35	1.06
Spring	2.96	0.00	6.75	0.00	0.55	2.19	2.21	1.11
Nitrate	Biomass	Coal	Sulfate	Incinerator	Traffic	Nitrate/Sulfat	Residential	Road
Overall	1.55	1.03	0.00	3.21	0.49	5.18	1.90	0.00
Summer	3.38	0.31	0.00	5.00	0.01	0.16	2.57	0.00
Autumn	0.53	0.17	0.00	2.01	0.17	1.83	0.71	0.00
Winter	1.71	1.11	0.00	2.86	1.30	13.76	1.81	0.00
Spring	1.62	2.31	0.00	3.95	0.38	3.97	2.96	0.00

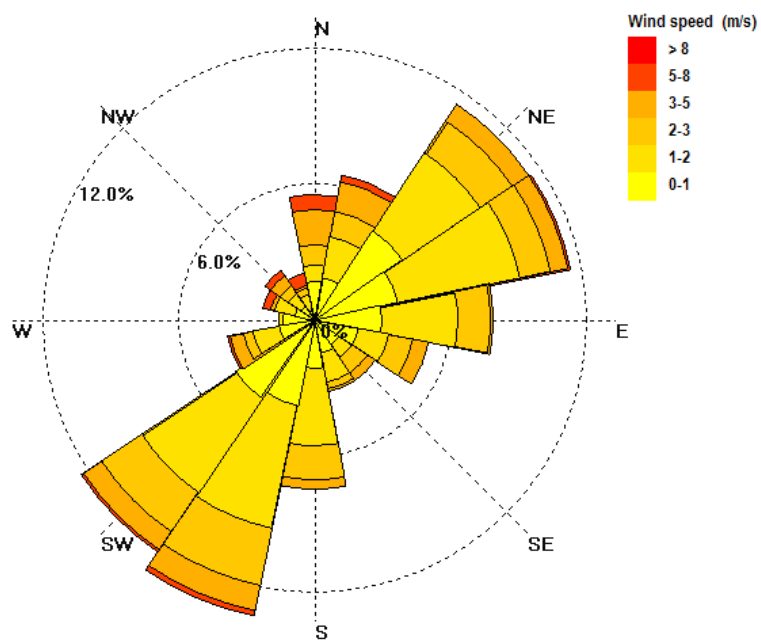
Table S3. Mean seasonal concentrations of the measured gaseous pollutants.

	O <sub>3</sub> (µg/m <sup>3</sup> )	NO (µg/m <sup>3</sup> )	NO <sub>2</sub> (µg/m <sup>3</sup> )	SO <sub>2</sub> (µg/m <sup>3</sup> )	CO (mg/m <sup>3</sup> )
Summer	62.3	9.3	53.3	34.0	1.4
Fall	41.3	32.3	58.6	12.5	0.9
Winter	17.4	92.3	77.1	62.9	3.1
Spring	32.1	47.7	94.0	49.0	1.9

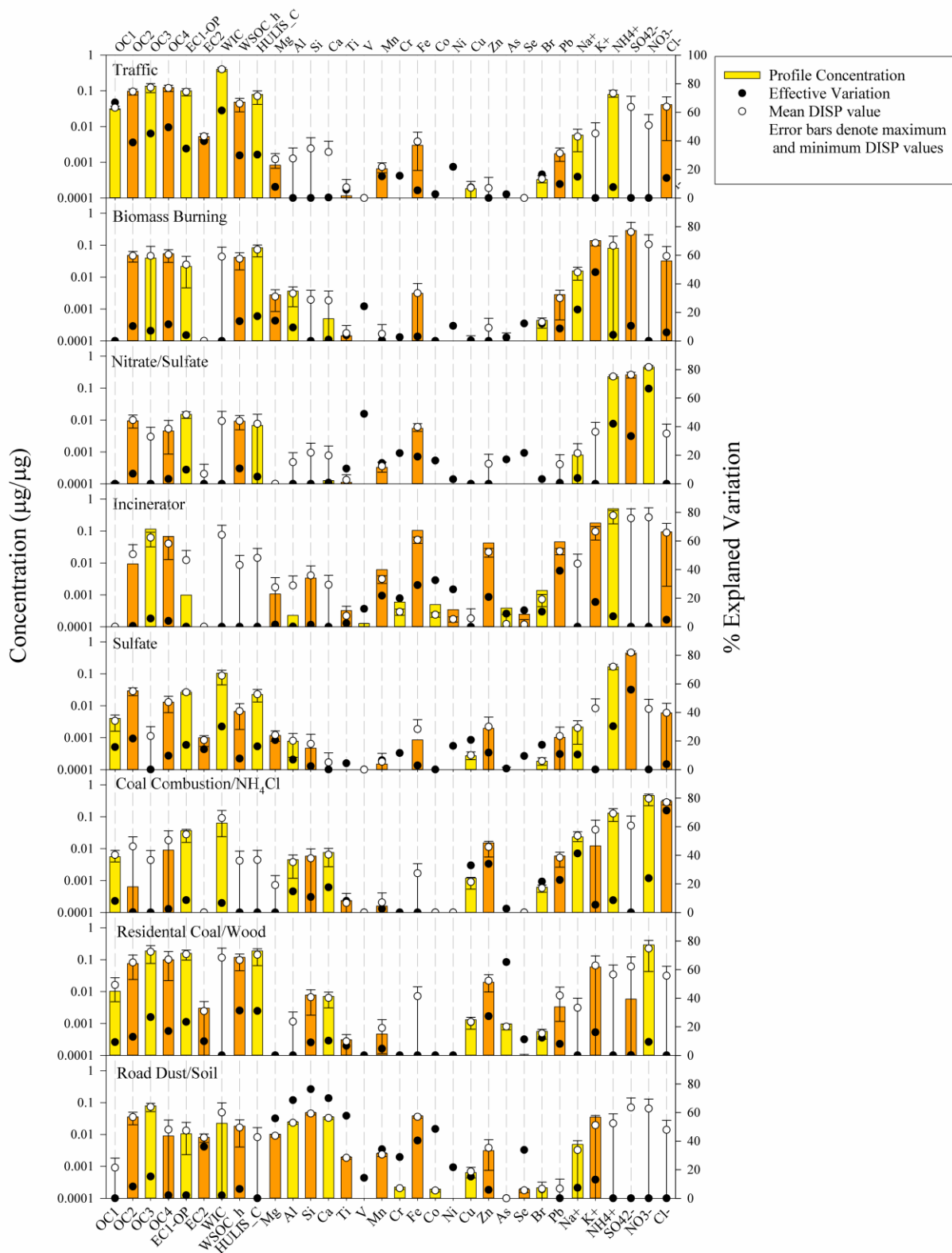
Table S4. CMAQ apportionment of primary sulfate sources ( $\mu\text{g}/\text{m}^3$ )*										
Period	Residential coal	Residential biofuel	transportation	power	industry	biomass open burning	total primary sulfate	observed sulfate	primary/observed	residential coal/obs
annual	1.63	0.31	0.080	0.18	2.42	0.015	4.63	28.77	0.158	0.057
summer	0.50	0.09	0.083	0.24	3.03	0.066	4.02	31.28	0.128	0.016
autumn	0.60	0.11	0.081	0.15	2.47	0.009	3.42	9.86	0.317	0.061
winter	4.89	0.92	0.12	0.24	3.02	0.00	9.19	68.87	0.133	0.071
spring	1.55	0.29	0.061	0.15	1.73	0.001	3.79	24.54	0.154	0.063

\*Results derived from the CMAQ modeling presented in Shi et al. (2017) and Li et al. (2019)

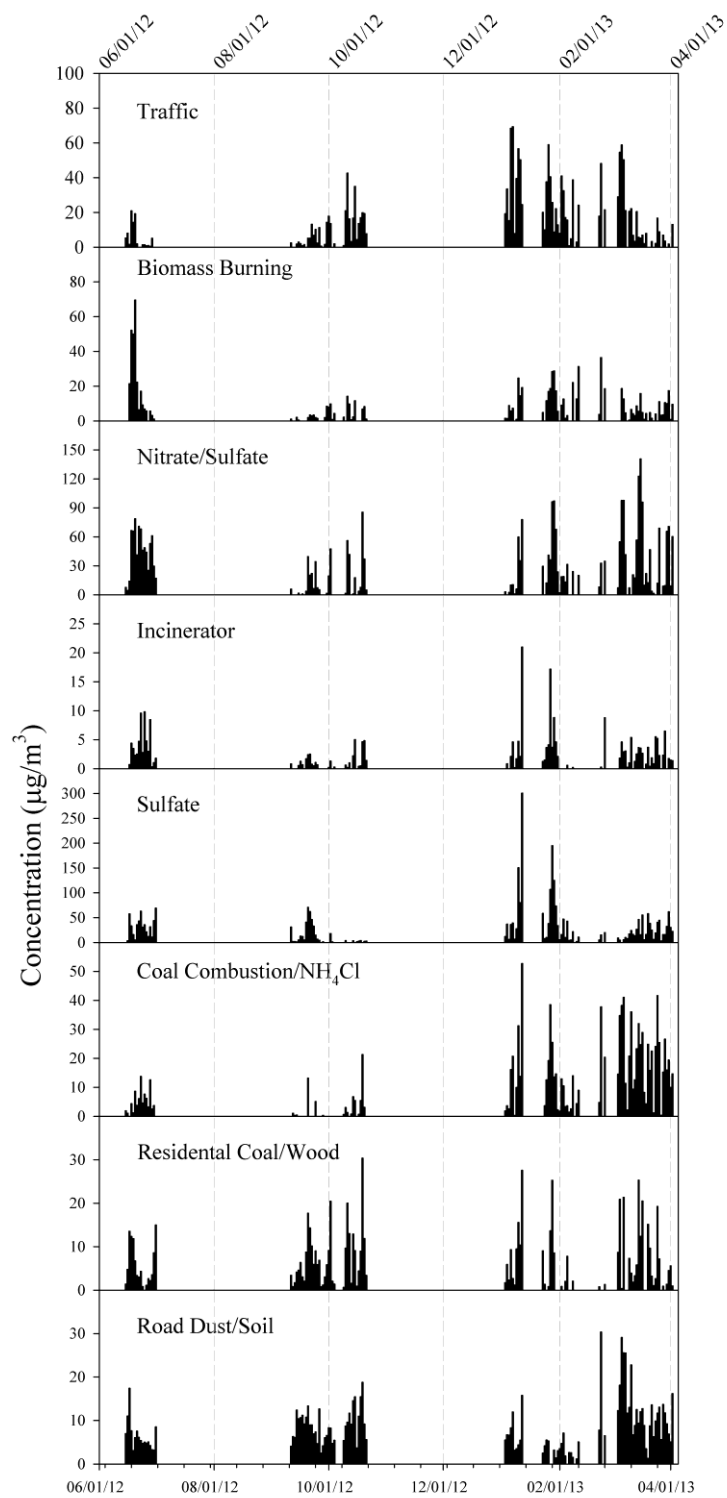




**Figure S1.** Wind rose for all of the days on which PM<sub>2.5</sub> samples were collected for analysis.



**Figure S2.** Profiles resolved from the data set that excluded the pollutant gases.



**Figure S3.** Time series of contributions from the factors resolved without the pollutant gases.

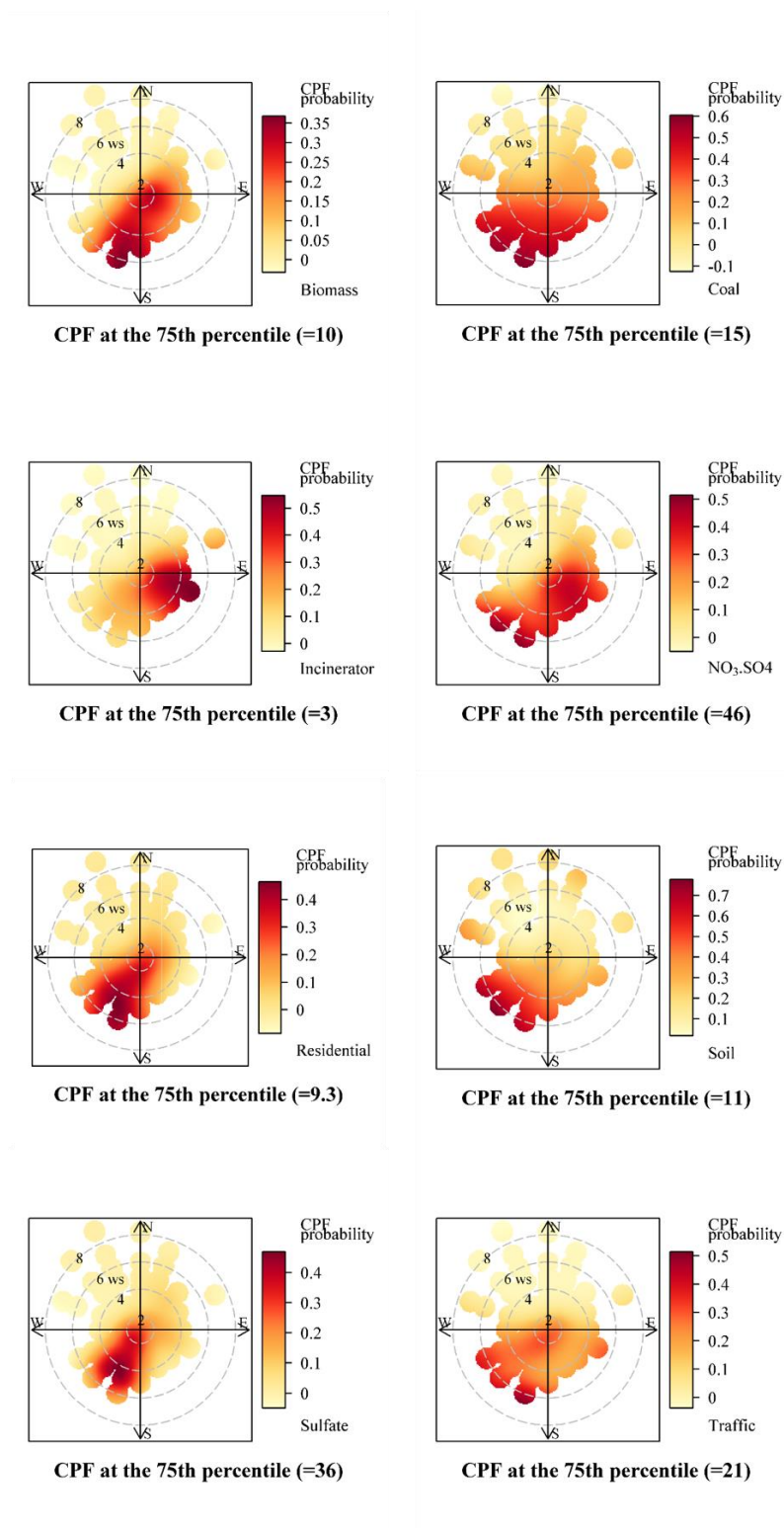


Figure S4. CCPF plots for the 8 factors resolved from the data without the pollutant gases. Wind speeds are in m/s. Values in the parentheses are the 75<sup>th</sup> percentile values in  $\mu\text{g}/\text{m}^3$ .

## References for the Supplemental Information

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