SupplementaryMaterials for:

Significant Contribution of Primary Sources to Water-Soluble Organic Carbon During Spring in Beijing, China

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Text S1. More detailed introduction of online measurements and related quality assurance and quality control protocols.

PILS-TOC. A long parallel plate denuder was placed in front of the particle inlet. Blank samples were collected at 0:00, 4:00, 8:00, 12:00, 16:00, and 20:00 each day to test and remove the background of the system. The particles were collected by PILS at a flow rate of 16.7 L/min into a liquid flow (1.3 ml/min) of deionized water [1], and the detection limit of the Total Organic Carbon (TOC) analyzer was 0.1 μg C/m^3. Briefly, ambient particles were captured by supersaturated vapor, grown to 3~5 μm in diameter size and collected by an inertial impactor. The resulting liquid passed through a filter and was injected into a TOC analyzer to measure WSOC concentration. The TOC analyzer measured WSOC concentration by converting it to carbon dioxide. Then carbon dioxide passed through semi-permeable membrane into deionized water (DI water) and its conductivity was measured. The concentration of aqueous carbon dioxide formed from the sample was proportional to the increase in conductivity of the DI water [2]. The background concentration was quantified by passing sample air through a Teflon filter to measure organic gases absorbed in the PILS and residual organic carbon in the DI water.

IGAC. IGAC is composed of three major parts, including a Wet Annular Denuder (WAD) to absorb gases into aqueous solution, a Scrub and Impact Aerosol Collector (SCI) to collect particles into solution and a sample analysis unit composed of two ion chromatographs for analyzing anions and cations. More detailed information about IGAC measurement could be found in Zhang et al. [3] The LiBr solution with a concentration of 0.14 ppm was added continuously to the impaction plate in SCI as an internal standard with a flow rate of 0.1mL/min, and analyzed by the IC system during the analysis of the sample solutions to check the stability of the IGAC instrument. The concentrations of water-soluble ions were calculated based on equation (1):

$$C_i = \frac{M_i}{V_1} \times V_2, \tag{1}$$

where C_i is the mass concentration of water-soluble ion i in the air (unit: μg/m^3); M_i is the mass concentration of ion i in the aqueous solution measured by ion chromatography (unit: μg/mL); V_1 is the sampling volume of air (unit: m^3); V_2 is the volume of aqueous solution (unit: mL).

IGAC was calibrated by nine concentration gradients of mixed standard solutions containing the target cations and anions (0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, and 2 ppm). During the study period, the slope of the linear fitting between the anions and cations was 1.20, with a correlation coefficient r 0.98 ($p < 0.05$).

Xact. Twenty-three elements (e.g., K, Ca, V, Cr, Cu, Zn, Ga, As, Mn, Fe, Co, Ni, Se, Ag, Cd, Sn, Sb, Au, Hg, Ba, Tl, Pb, and Bi) in PM$_{2.5}$ were measured by Xact 625 with a time resolution of 1-h. Ambient air was collected on a Teflon filter tape inside the instrument through a PM$_{2.5}$ cyclone inlet, with a constant flow rate of 16.7 L/min. Then the mass of metals collected on the tape was analyzed by energy-dispersive X-ray fluorescence (XRF) automatically. In this study, twelve of the element species (e.g., K, Ca, Ba, Cr, Mn, Fe, Cu, Ni, Zn, As, Se, and Pb) were finally used. The other metals (e.g., V, Co, Tl) were not used because their concentrations were mostly below the method detection limit (MDL). Before data collection of Xact, gas tightness and blank filter were tested. At the same time, the flow was calibrated while element concentration was calibrated by standard filter. A Pd rod was analyzed each hour to make sure the stability of Xact, as a part of an automatic internal quality control. Energy calibration test and energy level test were performed in the midnight from 00:00 to 00:30 each day in case there were any possible shifts of the Xact [4].

Text S2. The modified EC-tracer method for primary and secondary WSOC estimation and related uncertainties.

A modified EC-tracer method was applied to estimate the amount of primary and secondary WSOC, in which $(WSOC/EC)_{pri}$ ratio was used.

$$WSOC_{sec} = WSOC_{tot} - WSOC_{pri}, \quad (1)$$

$$WSOC_{pri} = (WSOC/EC)_{pri} \times EC, \quad (2)$$

where $WSOC_{sec}$ is secondary WSOC, $WSOC_{tot}$ is total WSOC, $WSOC_{pri}$ is primary WSOC, and $(WSOC/EC)_{pri}$ is the WSOC/EC ratio of aerosol from the primary emission. For the modified EC tracer method, it is assumed that EC is independent of $WSOC_{sec}$ and WSOC from non-combustion sources is negligible compared to $WSOC_{sec}$.

References

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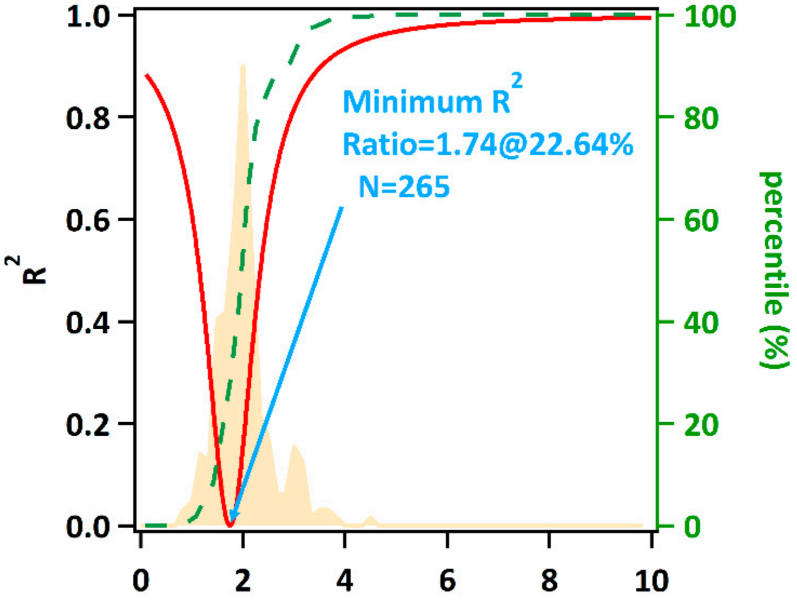

Figure S1. The $(WSOC/EC)_{pri}$ ratio determined by the MRS method. (Note: X-axis represents $(WSOC/EC)_{pri}$, and Y-axis represents R^2 of EC and secondary WSOC).

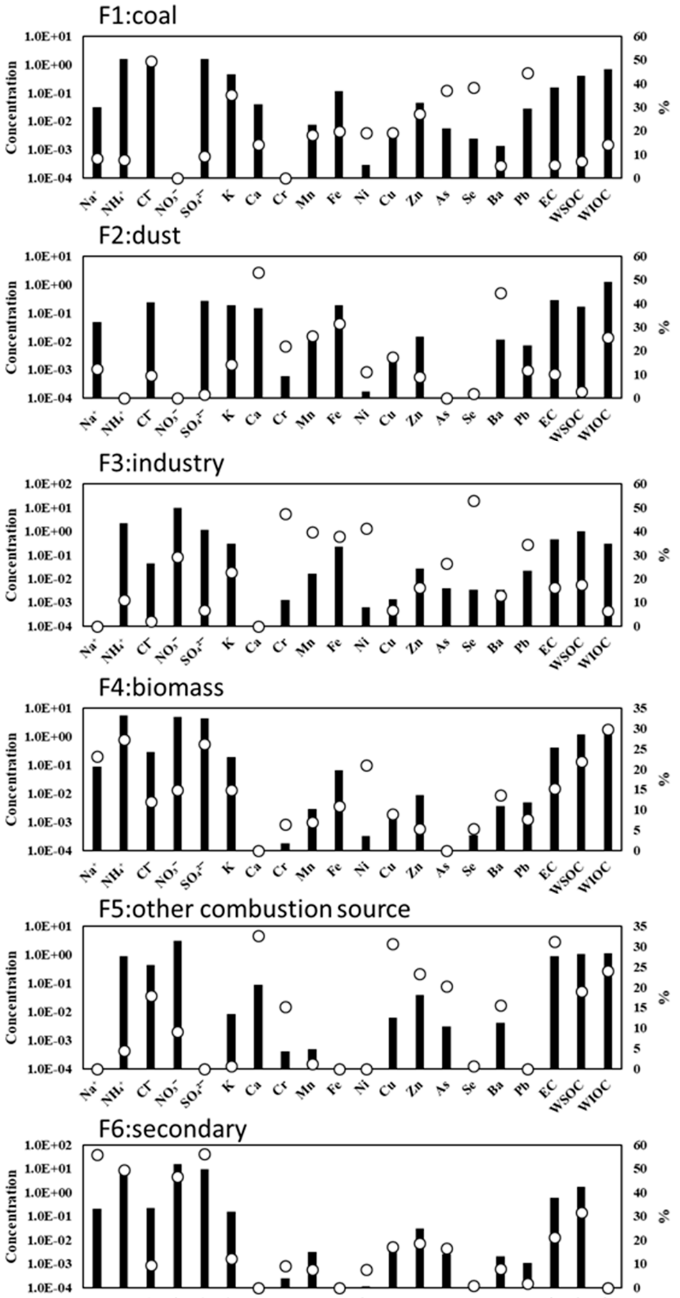

Figure S2. Source profiles of 6 factors identified by the PMF model as sources of WSOC during the study period

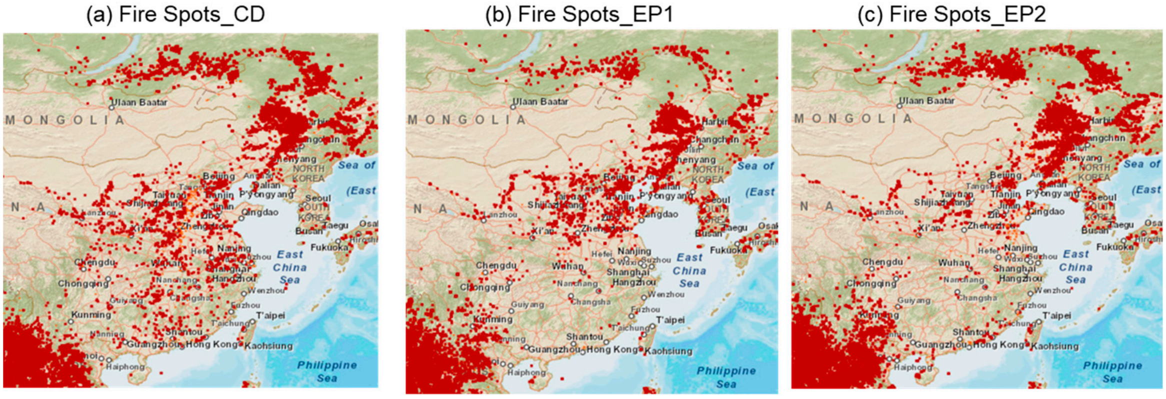

Figure S3. Fire maps during (a) CD, (b) EP1, and (c) EP2 provided by NASA FIRMS Web Fire Mapper (https://firms.modaps.eosdis.nasa.gov/map/).

Table S1 MDLs (μg/m^3) for each of the species in the PMF model

species	MDL	species	MDL
Cl^-	0.05	Ca	0.000902
NH_4^+	0.05	Cr	0.000288
NO_3^-	0.05	Fe	0.000759
SO_4^{2-}	0.04	Ni	0.000226
Na^+	0.04	Zn	0.000231
K	0.002366	Ba	0.000945
Mn	0.000283	Se	0.000141
As	0.000114	Pb	0.000218
Cu	0.000267	WSOC	0.1
EC	0.2	WIOC	0.1

Table S2 Pearson correlation coefficients of WSOC with different $PM_{2.5}$ components during the study period

	WSOC	EC	OC	K	Ca	Cr	Mn	Fe	Ni	Cu	Zn	As	Se	Ba	Pb	Na^+	NH_4^+	Cl^-	NO_3^-	SO_4^{2-}
WSOC	1.00																			
EC	0.95***	1.00																		
OC	0.97***	0.96***	1.00																	
K	0.88***	0.81***	0.85***	1.00																
Ca	0.61***	0.74***	0.73***	0.52***	1.00															
Cr	0.32***	0.44***	0.39***	0.25***	0.52***	1.00														
Mn	0.88***	0.88***	0.89***	0.89***	0.72***	0.56***	1.00													
Fe	0.87***	0.87***	0.89***	0.92***	0.74***	0.48***	0.97***	1.00												
Ni	0.74***	0.68***	0.67***	0.75***	0.36***	0.24***	0.69***	0.70***	1.00											
Cu	0.81***	0.85***	0.86***	0.75***	0.77***	0.40***	0.84***	0.81***	0.52***	1.00										
Zn	0.90***	0.87***	0.90***	0.88***	0.72***	0.36***	0.91***	0.91***	0.65***	0.87***	1.00									
As	0.93***	0.86***	0.89***	0.92***	0.55***	0.24***	0.86***	0.86***	0.76***	0.79***	0.91***	1.00								
Se	0.84***	0.74***	0.80***	0.96***	0.45***	0.26***	0.87***	0.90***	0.69***	0.69***	0.84***	0.88***	1.00							
Ba	0.79***	0.87***	0.87***	0.69***	0.91***	0.53***	0.85***	0.85***	0.49***	0.86***	0.84***	0.71***	0.63***	1.00						
Pb	0.84***	0.77***	0.82***	0.97***	0.54***	0.29***	0.90***	0.92***	0.66***	0.76***	0.89***	0.90***	0.95***	0.69***	1.00					
Na^+	0.52***	0.51***	0.51***	0.45***	0.32***	0.30***	0.54***	0.51***	0.23***	0.44***	0.44***	0.37***	0.46***	0.51***	0.45***	1.00				
NH_4^+	0.89***	0.76***	0.80***	0.86***	0.33***	0.21**	0.78***	0.78***	0.69***	0.63***	0.77***	0.85***	0.86***	0.57***	0.81***	0.48***	1.00			
Cl^-	0.71***	0.69***	0.75***	0.81***	0.66***	0.27***	0.78***	0.82***	0.53***	0.73***	0.84***	0.76***	0.76***	0.71***	0.79***	0.32***	0.67***	1.00		
NO_3^-	0.93***	0.83***	0.85***	0.90***	0.41***	0.24***	0.84***	0.85***	0.72***	0.69***	0.83***	0.89***	0.91***	0.64***	0.85***	0.54***	0.94***	0.70***	1.00	
SO_4^{2-}	0.88***	0.75***	0.78***	0.82***	0.31***	0.16*	0.76***	0.74***	0.73***	0.62***	0.76***	0.85***	0.82***	0.56***	0.75***	0.46***	0.88***	0.63***	0.92***	1.00

Note: *** p-value < 0.001, ** p-value < 0.01, * p-value < 0.05