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Measurement report: Oxidation potential of water-soluble aerosol components in the south and north of Beijing

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Calculation of absorption coefficient of BrC

The light absorption of water-soluble light-absorbing organic compounds (also known as brown carbon, BrC) were measured by an UV-Vis spectrophotometer equipped with a liquid waveguide capillary cell. During the measurement, the system was cleaned with ultrapure water (> 18.2 MΩ cm) after each sample analysis. After cleaning, for instrument calibration, the baseline was zeroed using the Spectra-Suite software so that zero absorption was recorded at all wavelengths for ultrapure water.

The light absorption data of BrC measured by the UV-Vis spectrophotometer equipped with a liquid waveguide capillary cell can be converted to the absorption coefficient (Abs) ($\mathrm{M\ m^{-1}}$) according to the following formula:

$$\mathrm{Abs}_{\lambda} = (\mathrm{A}_{\lambda} - \mathrm{A}_{700}) \times \frac{\mathrm{V}_{l}}{\mathrm{V}_{a} \times \mathrm{L}} \times \ln(10) \qquad \text{(S1)}$$

where Abs_{λ} is Abs of BrC at λ nm, A_{700} is the absorption at 700 nm, serving as a reference to account for baseline drift, V_{l} is the volume of water that the filter was extracted into, V_{a} is the volume of sampled air, and L is the optical path length (0.94 m). A factor of ln(10) is used to convert the log base 10 (recorded by UV–Vis spectrophotometer) to a natural logarithm to provide a base-e absorption coefficient.

ICP-MS analysis

For ICP-MS analysis, a seven-point calibration curve (i.e., 1, 2, 5, 10, 20, 50, 100 $\mu\mathrm{g\ L^{-1}}$) was established for each targeted element, and the regression coefficients for all elements were > 0.999. For the analysis, $^{103}\mathrm{Rh}$ and $^{185}\mathrm{Re}$ were added as internal standards at a concentration of 10 $\mu\mathrm{g\ L^{-1}}$ in 2% $\mathrm{HNO_3}$. At least one blank sample was analyzed for every 10 ambient samples, following the same procedures as for ambient samples. All data reported in this study were corrected for the blanks. The accuracy was estimated by analyzing the reference material GBW07406 (GSS-6). The differences between the measured and certified values ranged from -20% to 15% for the fourteen elements.

GC-MS analysis

Half of a 47 mm filter sample was ultrasonically extracted with a mixture of dichloromethane and methanol (2:1, v/v) for 15 min and repeated three times. The extracts were purified by quartz wool packed in a Pasteur pipette and then evaporated with a rotary evaporator to ~ 0.5 mL and dried with a gentle stream of nitrogen.Then, 50 μL of N,Obis(trimethylsilyl)trifluoroacetamide (BSTFA-TMCS; Fluka Analytical, 99 %) and 10 μL of pyridine were added and heated for 3 h at 70 ℃ for silylation. After reaction, 140 μL of n-hexane was added to dilute the derivatives. Finally, a 2 μL aliquot of the derivatized extracts was introduced into the GC–MS (Agilent Technologies, Santa Clara, CA, USA), which was equipped with a DB-5MS column (30 m × 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific), an electron impact (EI) ionization source (70 eV) and a GC inlet of 280 ℃. The GC oven temperature was held at 50 ℃ for 2 min, ramped up to 120 ℃ at a rate of 15 ℃ min^{-1} and finally reached 300 ℃ at a rate of 5 ℃ min^{-1} (held for 16 min). For the quantification of target organic compounds, an external standard method was used through daily calibration with working standard solutions. Also, for every 10 samples, a procedural blank and a spiked sample (i.e., ambient sample spiked with known amounts of standards) were measured to check the interferences and recoveries. The measured recoveries were > 80 %, except for phthalic acid (~ 70%), and the relative standard deviations (RSDs) were < 10 % for measured organic compounds. The method detection limits were 0.04-0.1 ng m^{-3} for nonpolar compounds and 0.06-0.2 ng m^{-3} for polar compounds.

PMF analysis

The PMF receptor model has been widely used to quantify the sources of $PM_{2.5}$ oxidative potential. In this study, the concentrations and uncertainties of 14 trace elements, 8 organic markers and DTT_v were input into PMF model. The uncertainties of species were calculated following Liu et al. (2017). For species with concentrations less than the method detection limit (MDL), the concentrations were replaced as MDL/2 and the uncertainties (Unc) were calculated by the following equation:

$$\mathrm{Unc} = \frac{5}{6} \times \mathrm{MDL} \qquad \text{(S2)}$$

For species with concentrations larger than the MDL, the uncertainties were calculated as the MDL and a relative error (20%) summed in quadrature,

$$\mathrm{Unc} = \sqrt{(\text{Error Fraction} \times \text{concentration})^2 + (0.5 \times \mathrm{MDL})^2} \qquad \text{(S3)}$$

All data input into PMF model has a signal-to-noise ratio (S/N) greater than 2. PMF model is based on the following equation:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \qquad \text{(S4)}$$

Where x_{ij} refers to the concentration of the i_{th} sample and the j_{th} substance; p represent the number of factors; g_{ik} is the relative contribution of factor k to i_{th} sample; f_{kj} refers to the profile factor of each source for the j_{th} substance, and e_{ij} is the residual error for the i_{th} sample and the j_{th} substance. PMF solves equation S3 and derive the most appropriate non-negative factor profiles and contributions by minimizing the objective function (Q):

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{e_{ij}}{u_{ij}}\right)^2 \qquad \text{(S5)}$$

Where n refers to the number of samples; m is the number of species, and u_{ij} is the uncertainty of the measured concentration for the i_{th} sample and the j_{th} specie.

In this study, the PMF solutions from five to seven factors were examined, the oil factor mixed with vehicle emissions factor in the five-factor solution, and there was no new reasonable factor when increasing the factor number above 6 in the PMF analysis (Figure S6). Therefore, the six-factor solution was adopted (Figure S7). The Q/Q_{exp} value for six-factor solution was below than four, which is acceptable.

Table S1. *F* matrix elements constrained in the ME-2/chemical species 6 factors solution. The 0 value denote the $f_{h,j}$ values constrained in ME-2, while hyphens denote unconstrained elements.

Species	Biomass burning	Coal Burning	Traffic-related	Secondary Formation	Dust	Oil combustion
DTTv	-	-	-	-	-	-
Ti	-	-	-	0	-	-
V	-	-	-	0	-	-
Cr	-	-	-	0	-	-
Mn	-	-	-	0	-	-
Fe	-	-	-	0	-	-
Co	-	-	-	0	-	-
Ni	-	-	-	0	-	-
Cu	-	-	-	0	-	-
Zn	-	-	-	0	-	-
As	-	-	-	0	-	-
Sr	-	-	-	0	-	-
Cd	-	-	-	0	-	-
Ba	-	-	-	0	-	-
Pb	-	-	-	0	-	-
Picene	-	-	-	0	0	-
Hopanes	0	-	-	0	0	0
Galactosan	-	0	0	0	0	0
Mannosan	-	0	0	0	0	0
Levoglucosan	-	0	0	0	0	0
o-ph	0	0	0	-	0	0
m-ph	0	0	0	-	0	0
p-ph	0	0	0	-	0	0

Table S2. Average values and standard deviation (Std) of measured parameters in the southern and northern of Beijing.

Compounds	South		North	
	Average	Std	Average	Std
$PM_{2.5}$ (μg m^{-3})	122	49	62	28
DTTv (nmol min^{-1} m^{-3})	3.9	0.9	3.5	1.2
DTTm (pmol min^{-1} $μg^{-1}$)	36	14	65	28
WSOC (μg m^{-3})	8.1	5.0	4.0	2.0
Abs_{365} (M m^{-1})	20	13	6.8	5.4
4-nitrophenol (4NP) (ng m^{-3})	62	40	21	13
2-methyl-4-nitrophenol (2M4NP) (ng m^{-3})	25	17	7.7	4.7
3-methyl-4-nitrophenol (3M4NP) (ng m^{-3})	22	16	7.1	4.0
4-nitrocatechol (4NC) (ng m^{-3})	58	45	13	18
3-methyl-5-nitrocatechol (3M5NC) (ng m^{-3})	37	28	7.0	8.3
4-methyl-5-nitrocatechol (4M5NC) (ng m^{-3})	23	19	4.2	4.6
4-nitro-1-naphthol (4N1N) (ng m^{-3})	12	8.2	3.1	3.0
Picene (ng m^{-3})	6.3	4.7	3.2	2.8
Hopanes (ng m^{-3})	13.7	9.9	2.3	1.5
Galactosan (ng m^{-3})	61.8	45.1	6.0	4.6
Mannosan (ng m^{-3})	37.4	29.7	4.1	2.8
Levoglucosan (ng m^{-3})	474.2	318.2	90.3	70.1
Phthalic acid (*o*-ph) (ng m^{-3})	69.8	62.7	28.4	32.2
Isophthalic acid (*m*-ph) (ng m^{-3})	2.6	2.9	0.7	0.6
Terephthalic acid (*p*-ph) (ng m^{-3})	85.1	57.8	12.6	10.5
Total elements (ng m^{-3})				
Ti	200	98	131	64
V	4.1	2.0	2.9	1.4
Cr	24	4.9	17	3.7
Mn	80	27	56	20
Fe	1717	811	1267	574
Co	0.8	0.3	0.6	0.3
Ni	3.5	0.7	3.4	0.7
Cu	79	66	25	24
Zn	225	120	131	78
As	11	9.6	6.0	5.7
Sr	27	12	16	6.8
Cd	1.6	1.0	0.7	0.5
Ba	71	24	69	12
Pb	65	43	25	16

Table S3. DTT_v values in the south and north of Beijing and their sources contributions.

	South	North
DTT_v (nmol min^{-1} m^{-3})	3.9	3.5
Sources contribution to DTT_v (%)		
Biomass burning	25	8
Coal burning	15	20
Traffic-related	39	52
Secondary formation	17	13
Dust	2	3
Oil combustion	2	4
Sources contribution to DTT_v (nmol min^{-1} m^{-3})		
Biomass burning	0.98	0.29
Coal burning	0.59	0.70
Traffic-related	1.5	1.8
Secondary formation	0.67	0.46
Dust	0.08	0.11
Oil combustion	0.06	0.14

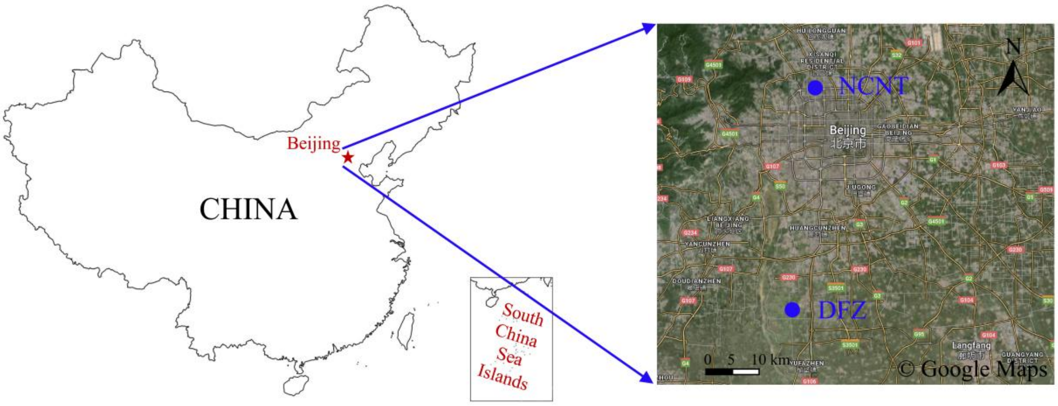

Figure S1. Map of the sampling sites. NCNT and DFZ are abbreviations for the north (the National Center for Nanoscience and Technology) and south (the Dingfuzhuang village, Daxing district) sites of Beijing, China, respectively. The left panel from Ministry of Natural Resources of China, and the right panel from Google Maps.

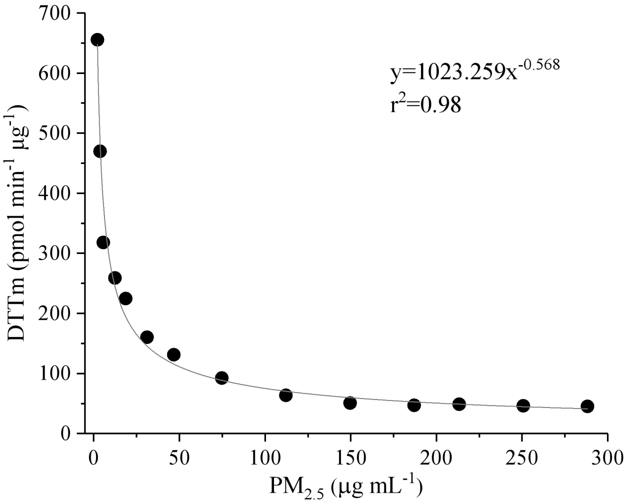

Figure S2. Measured DTTm response as a function of $PM_{2.5}$ concentration in the extraction solution. The concentrations of soluble Cu and Mn in this sample were 23.7 and 23.4 ng m^{-3}, respectively.

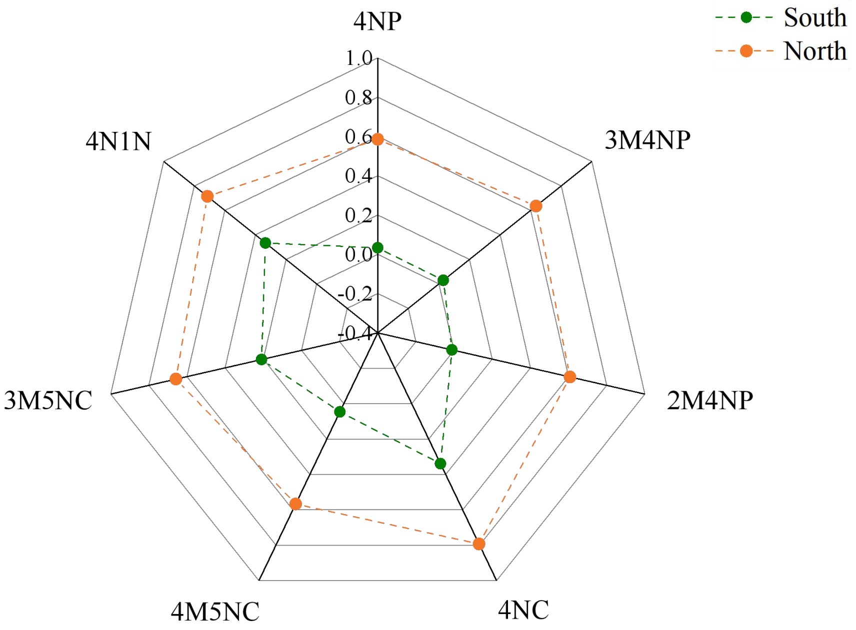

Figure S3. Correlation coefficients between DTTv and NACs in the south and north of Beijing.

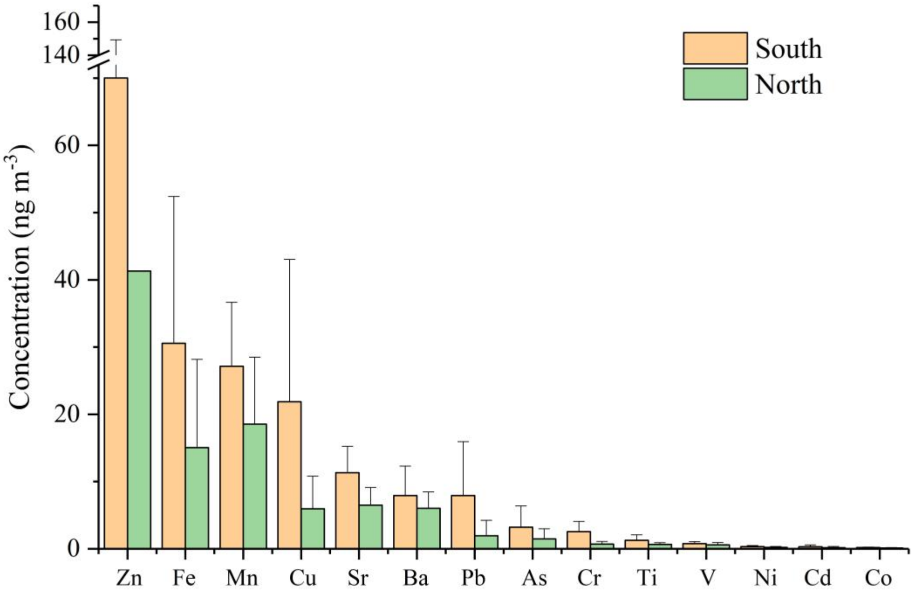

Figure S4. Concentrations of soluble elements in the south and north of Beijing.

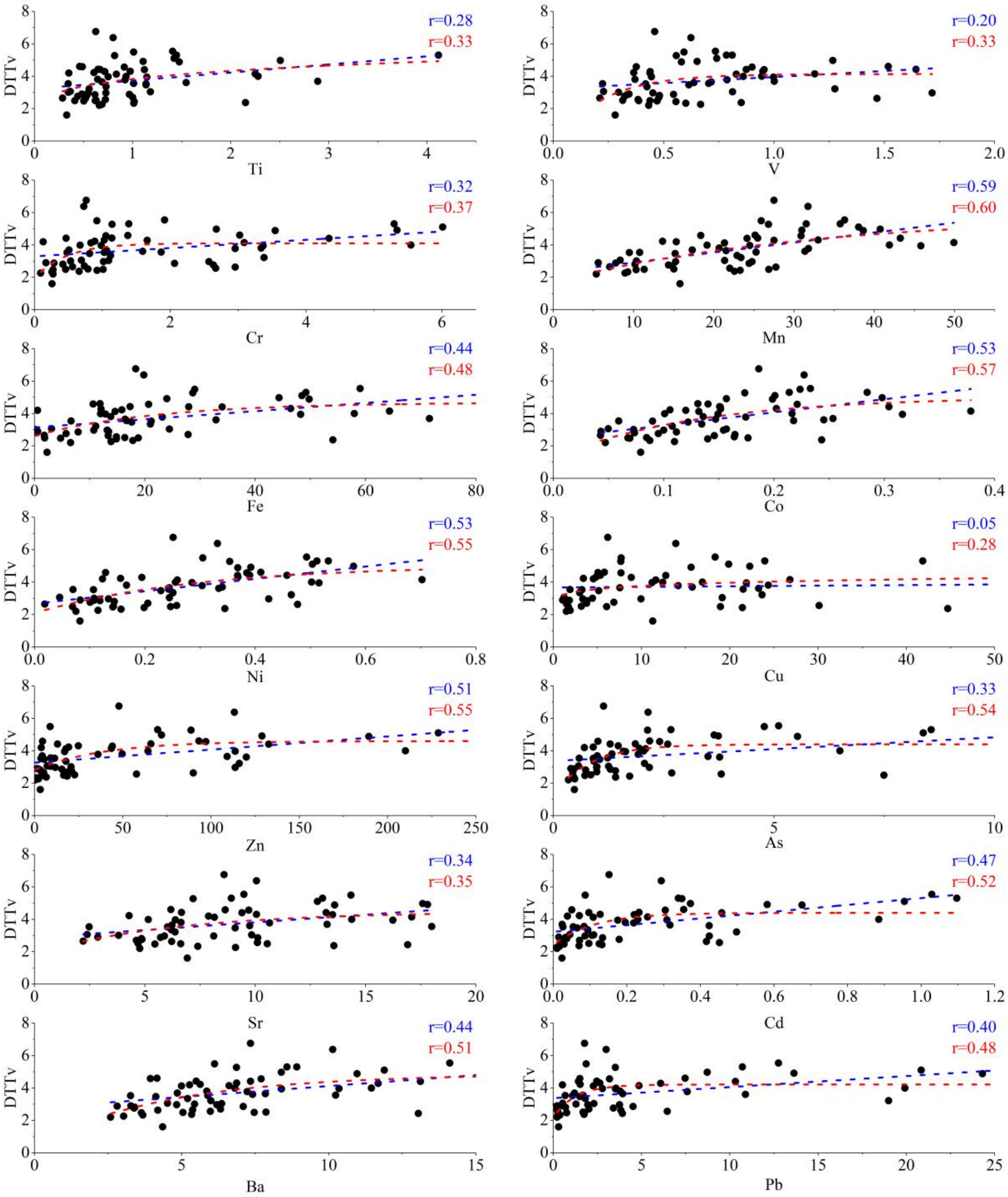

Figure S5. Relationship between soluble trace elements concentration (ng m^{-3}) and DTT$_v$ (nmol min^{-1} m^{-3}).

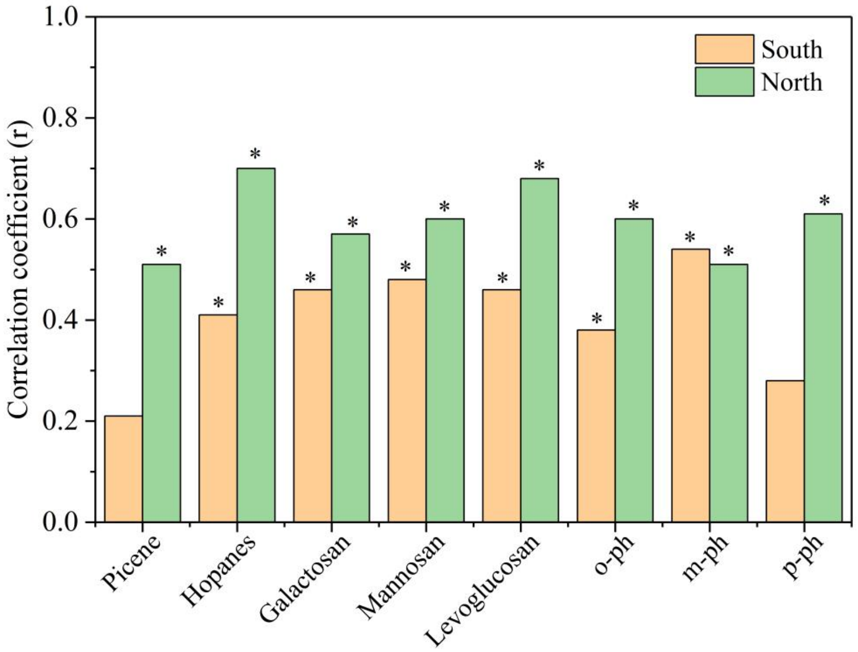

Figure S6. Correlation coefficients between DTTv and organic markers in the south and north of Beijing (* indicates correlation is significant at the 0.05 level).

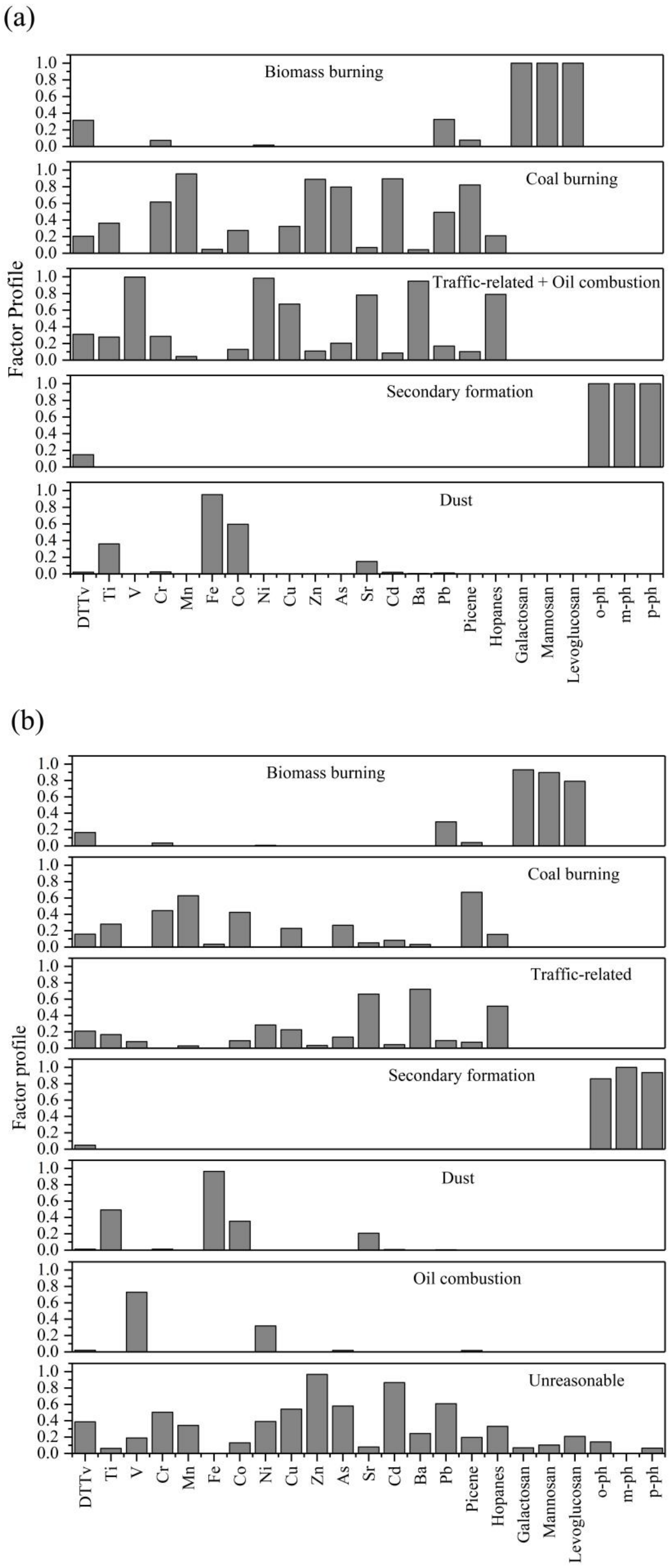

Figure S7. Factor profiles for the resolved (a) five-factor solution, and (b) seven-factor solution.

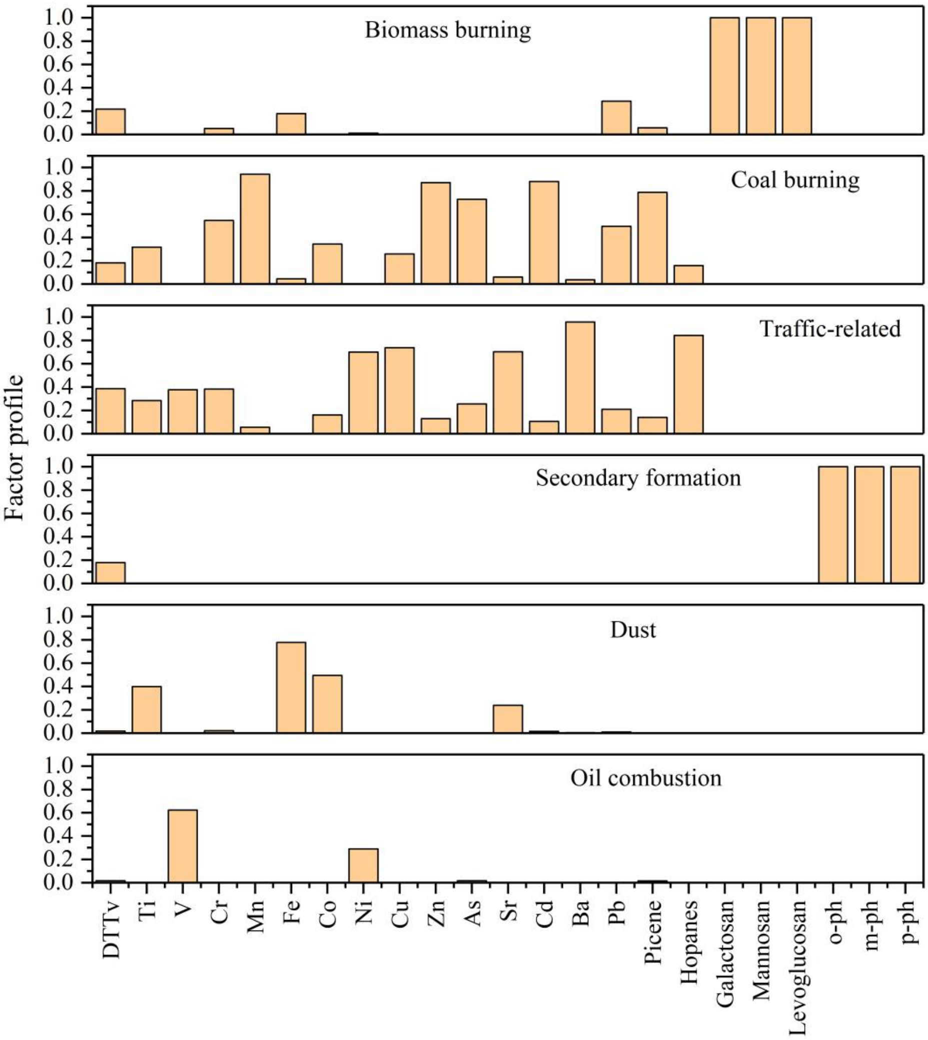

Figure S8. Factor profiles for the resolved six-factor solution.

References

Liu, Y., Yan, C. Q., Ding, X., Wang, X. M., Fu, Q. Y., Zhao, Q. B., Zhang, Y. H., Duan, Y. S., Qiu, X. H., and Zheng, M.: Sources and spatial distribution of particulate polycyclic aromatic hydrocarbons in Shanghai, China, Sci. Total Environ., 584-585, 307-317, https://doi.org/10.1016/j.scitotenv.2016.12.134, 2017.