Characteristics, primary sources and secondary formation of water soluble organic aerosols in downtown Beijing

Supporting Information

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S1 Chemical analysis of water-soluble ions and water-soluble organic carbon (WSOC)

To analyze the concentrations of water-soluble ions and water-soluble organic carbon (WSOC), a punch of each sampled filter was cut into pieces and extracted with 40 mL ultrapure water (>18.2 MΩ) for 30 min, then passed through a 0.45 μm PTFE filter. Five cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and four anions (Cl^-, NO_3^-, SO_4^{2-}, $C_2O_4^{2-}$) were measured using the ion chromatography (Dionex 600), with methanesulfonic acid (MSA) solution as the cationic eluent and potassium hydroxide (KOH) solution as anionic eluent. The concentration of WSOC was measured by a TOC analyzer (Shimazdu TOC-L CPN). The standard solution of the total carbon (TC) was made by potassium acid phthalate ($C_8H_5KO_4$), and that of inorganic carbon (IC) was made by sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$). Total organic carbon (TOC) was calculated as total carbon minus inorganic carbon.

S2 The parameter settings of GC/MS/MS for analyzing organic tracers

The derivatives were immediately analyzed by a Shimadzu TQ8040 gas chromatography triple quadrupole mass spectrometry (GC/MS/MS). A JA-5MS capillary column (30 m × 0.25 mm i.d., film thickness 0.25 μm) was used as the GC column and helium was used as the carrier gas (1.0 mL min^{-1}). The injector was set splitless at a temperature of 290 °C. The programmed oven temperature increased from 70 °C to 150 °C at 2 °C min^{-1}, then to 200 °C at 5 °C min^{-1}, then to 300 °C at 25 °C min^{-1}, and stayed at 300 °C for 6 min. The MS was operated in EI mode at 70 eV with a scan range of 50-650 amu.

Table S1 WSOC, OC concentrations and WSOC/OC ratios in $PM_{2.5}$ Beijing in recent years.

Sampling period	WSOC (μg m^{-3})	OC (μg m^{-3})	WSOC/OC	OC method*	Reference
2017 Winter	11.71 ± 13.92	20.56 ± 21.89	0.52 ± 0.08	IMPROVE (TOR)	This study
2017 Spring	4.40 ± 2.34	8.70 ± 3.12	0.49 ± 0.12		
2017 Summer	4.66 ± 2.46	7.75 ± 3.91	0.60 ± 0.11		
2017 Autumn	4.77 ± 2.83	9.71 ± 3.69	0.46 ± 0.12		
2016 Spring	3.8 ± 3.8[a]	7.9 ± 7.4	0.48	Optical transmittance	Yang et al. (2019)
2016 Summer	2.3 ± 0.9[a]	3.4 ± 1.0	0.68		
2016 Autumn	4.8 ± 4.1[a]	7.9 ± 7.6	0.61		
2016 Winter	10.0 ± 10.1[a]	20.7 ± 16.2	0.49		
2013 Autumn	Not mentioned	11.4	0.70 ± 0.27	IMPROVE (TOR)	Zhao et al. (2018)
2013 Winter		19.4	0.49 ± 0.11		
2014 Spring		8.53	0.56 ± 0.07		
2014 Summer		5.29	0.58 ± 0.10		
2013-2014 Winter	12.8	29.1	0.46	IMPROVE-A	Huang et al. (2020)
2013 Winter	10.8 ± 3.1	32.9 ± 16.8	0.39 ± 0.16	IMPROVE-A (TOT)	Yan et al. (2015)
2013 Summer	6.4 ± 2.2	9.7 ± 2.9	0.66 ± 0.06		
2012 Summer	4.4 ± 3.6	8.5 ± 5.2	0.52	IMPROVE-A (TOR)	Li et al. (2019a)
2012 Autumn	5.2 ± 4.0	10.3 ± 7.4	0.50		
2013 Winter	10.3 ± 9.8	28.9 ± 22.0	0.36		
2013 Spring	5.9 ± 4.9	14.6 ± 10.8	0.40		
2011-2012 Winter	Not mentioned	Not mentioned	0.36 ± 0.05[b] 0.44 ± 0.05[c] 0.47 ± 0.05[d]	IMPROVE-A (TOT)	Cheng et al. (2015)
2011 Summer	4.48	13.55	0.33	IMPROVE (TOR)	Xiang et al. (2017)
2011 Autumn	5.82	25.42	0.25		
2011 Winter	5.53	28.16	0.20		
2012 Spring	3.90	16.57	0.27		
2012 Summer	5.81	16.54	0.34		
2011 Summer	7.8 ± 4.4	12.0 ± 6.3	0.65	IMPROVE-A (TOT)	Cheng et al. (2013)
2011-2012 Winter	11.2 ± 8.2	24.6 ± 17.1	0.46		
2010 Fall	8.6 ± 6.4	20.4 ± 15.4	0.42	IMPROVE (TOT)	Du et al. (2014)
2010 Winter	8.0 ± 6.7	20.6 ± 16.1	0.39		
2011 Spring	4.7 ± 3.1	10.2 ± 6.8	0.46		
2011 Summer	6.7 ± 4.4	10.7 ± 6.2	0.61		
2011 Fall	8.6 ± 6.1	19.7 ± 15.4	0.44		
2009 Spring	6.7 ± 1.8	13.7 ± 4.4	0.49	Not mentioned	Tao et al.(2016)

2009 Summer	3.2 ± 1.1	11.1 ± 1.8	0.29		
2009 Autumn	7.7 ± 5.0	17.8 ± 5.6	0.43		
2010 Winter	7.7 ± 3.6	24.9 ± 15.6	0.31		
2009 Winter	7.28	27.7 ± 15.4[e]	0.26	IMPROVE-A (TOR)	Cheng et al. (2011)
		30.9 ± 16.3[f]	0.24		
		32.6 ± 18.6[e]	0.22	IMPROVE-A (TOT)	
		36.1 ± 19.5[f]	0.20		
2009 Summer	3.36	7.2 ± 2.4[e]	0.48	IMPROVE-A (TOR)	
		9.4 ± 2.7[f]	0.36		
		8.8 ± 3.3[e]	0.38	IMPROVE-A (TOT)	
		11.4 ± 3.6[f]	0.30		

[*] The thermal-optical reflectance (TOR) method and thermal-optical transmittance (TOT) method are two different charring correction methods to determine the split of OC and EC. The transmittance-defined EC is the carbon measured after the filter transmittance returns to its initial value in the He/O_2 atmosphere, whereas the reflectance-defined EC is the carbon measured after the filter reflectance returns to its initial value (Cheng et al., 2011).

[a] In Yang et al. (2019), the concentrations of WSOC were measured by UV/VIS absorption (at wavelengths of about 250 nm)

[b,c,d] In Cheng et al. (2015), "b" refers to the constructed $PM_{2.5}$ below 30 μg m^{-3}, "c" between 30 μg m^{-3} and 90 μg m^{-3}, and "d" above 90 μg m^{-3}.

[e,f] In Cheng et al. (2011), "e" was measured using the denuded quartz filter and "f" was measured using the un-denuded (bare) quartz filter.

Table S2 Spearman correlation coefficients between the SOA tracers and meteorological parameters, O_3, aerosol acidity, and aerosol liquid water content (LWC) in different seasons in Beijing.

Compounds	Seasons	T	RH	WS	SR	O_3	Acidity	LWC
WSOC/OC	Whole year	0.296**	0.290**	-0.142	0.021	0.152	0.480**	0.387**
	Winter	0.495**	0.550**	-0.298	-0.508	-0.267	0.655**	0.684**
	Spring	-0.149	0.640**	-0.317	-0.762**	-0.424*	0.784**	0.680**
	Summer	0.273	-0.066	-0.053	-0.082	0.081	-0.112	0.063
	Autumn	0.469**	0.365*	-0.074	-0.068	-0.073	0.466**	0.619**
Phthalic acid	Whole year	0.048	0.212*	-0.198*	-0.137	-0.146	0.431**	0.452**
	Winter	0.389*	0.657**	-0.621**	-0.648*	-0.645**	0.747**	0.869**
	Spring	-0.158	0.681**	-0.300	-0.865**	-0.486**	0.857**	0.768**
	Summer	0.714**	-0.597*	0.308	0.186	0.653**	0.136	-0.321
	Autumn	0.549**	0.325	-0.082	-0.103	-0.013	0.503**	0.579**
4-Methyl-5-nitrocatechol	Whole year	-0.780**	0.051	-0.229*	-0.691**	-0.841**	0.222*	0.227*
	Winter	0.201	0.688**	-0.712**	-0.618*	-0.766**	0.704**	0.875**
	Spring	-0.516**	0.880**	-0.553**	-0.932**	-0.685**	0.773**	0.816**
	Summer	-	-	-	-	-	-	-
	Autumn	-0.259	0.211	-0.281	-0.044	-0.504**	0.042	0.186
2-Methylerythritol	Whole year	0.595**	0.545**	-0.343**	0.211	0.333**	0.798**	0.562**
	Winter	0.304	0.686**	-0.624**	-0.530	-0.679**	0.719**	0.868**
	Spring	-0.079	0.563**	-0.440*	-0.524*	-0.535**	0.668**	0.545**
	Summer	0.657**	-0.399*	0.249	0.343	0.563**	0.247	-0.074
	Autumn	0.255	0.371*	-0.243	0.109	-0.253	0.450**	0.520**
3-Hydroxyglutaric acid	Whole year	0.626**	0.534**	-0.299**	0.212	0.372**	0.766**	0.576**
	Winter	0.495**	0.649**	-0.640**	-0.653*	-0.615**	0.778**	0.844**
	Spring	-0.146	0.672**	-0.338	-0.715**	-0.429*	0.854**	0.668**
	Summer	0.533**	-0.293	0.059	0.186	0.536**	-0.013	0.108
	Autumn	0.482**	0.340	-0.002	0.018	0.012	0.400*	0.613**
cis-Pinonic acid	Whole year	0.591**	0.032	-0.092	0.178	0.348**	0.249**	0.111
	Winter	0.368*	0.577**	-0.650**	-0.473	-0.660**	0.646**	0.790**
	Spring	0.263	0.232	-0.128	-0.785**	-0.141	0.566**	0.390*
	Summer	-0.007	-0.204	-0.149	0.236	-0.139	0.431*	-0.336
	Autumn	0.778**	-0.426*	0.306	0.344	0.537**	-0.021	-0.161

T: temperature; RH: relative humidity; WS: wind speed; SR: solar radiation; LWC: liquid water content.

Level of significance: *: $p<0.05$; **: $p<0.01$.

Reference

Cheng, Y., He, K., Duan, F., Zheng, M., Du, Z., Ma, Y., and Tan, J.: Ambient organic carbon to elemental carbon ratios: Influences of the measurement methods and implications, Atmos. Environ., 45, 2060-2066, doi:10.1016/j.atmosenv.2011.01.064, 2011.