Supplementary of

Characterizing water solubility of fresh and aged secondary organic aerosol in $PM_{2.5}$ with the stable carbon isotope technique

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Text S1: PMF model and results

In this study, the PMF model (EPA PMF v5.0,) was employed to identify the sources of TC and WSOM. The detailed fundamental principle of this model can be found in Paatero et al.(1994) (Paatero and Tapper 1994). The mass concentration and uncertainty values of seventeen indicative chemical components (OM, EC, NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, Na, Mg, Al, K, Ca, V, Ni, Cd, Fe, Zn, and Pb) were put into this model to calculate the contributions of different sources to TC. The information on the measurement of the carbonaceous fractions is described in the main text. In addition, an Ion Chromatography Analyser (ICS-2500, Dionex; Sunnyvale, California, USA) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Aurora M90; Bruker, Germany) were used for the mass concentration analysis of water-soluble ions and metal elements respectively. Ten factors (vehicle emissions, ship emissions, aged sea salt, construction dust, fugitive dust, coal combustion, industrial emissions, biomass burning, secondary sulfate, and secondary nitrate) were identified, as shown in Fig. S2. SOA was then estimated from the OM fraction in both secondary sulfate and secondary nitrate factors. To compare with BSIM results, the source apportionment of TC was merged into three sources, including SOA, traffic emission, and biomass burning (Fig. S3) (Zong et al., 2018). The industrial emission source and coal combustion source were not included because of their little contribution to carbonaceous fraction. The remaining eight sources were then reapportioned and then combined according to the contribution to OC and EC. Specifically, the contributions of vehicle and ship emissions to EC and OC were attributed to the traffic source. The contributions of secondary sulfate, secondary nitrate, and aged sea salt sources to OC were all attributed to the SOA. The contributions of biomass burning source to OC were attributed to the BB (biomass burning) source. The mass concentration and uncertainty values of five species (CO_2^+, $C_4H_9^+$, $C_2H_4O_2^+$, WSOC, and WSOO) were put into the PMF model to calculate the contribution of three sources (BBOA

(biomass burning organic aerosol), LO-OOA (less-oxidized oxygenated OA), MO-OOA (more-oxidized oxygenated OA)) to WSOM (Fig. S4).

Text S2: Sampling of potential emission sources of carbonaceous aerosol

$PM_{2.5}$ samples of four sources were collected from ambient air and simulation experiments to measure the $\delta^{13}C$ values of TC and WSOC in this study. We collected $PM_{2.5}$ samples from two tunnel sites (Mount Tanglang tunnel and Jiuweiling tunnel), which can comprehensively reflect the vehicle emissions level to ambient air in Shenzhen because of its specificity of the environment. Two medium-flow samplers (KC-120H model, Qingdao Laoshan, 100 L/min) were used in this sampling process. The lengths of those two tunnels were 1711 m and 1447 m, representing the emission characteristics of diesel and petrol vehicles in Shenzhen respectively. General information about the number of samples and sampling time at each tunnel are provided in Table S4 and S5. Specifically, six samples were obtained from 23:00 to 02:10 and 02:30 to 05:30 on 13-18 October 2014 at the Mount Tanglang tunnel site. Additional eight samples were subsequently collected at different periods (peak and off-peak traffic periods in both daytime and night) on 20-22 January 2015 at the junction of one side of Mount Tanglang tunnel, and the sampling durations ranged from 2.5 to 11.5 hours. A total of 11 samples were obtained at the Jiuweiling tunnel site. The peak and off-peak traffic periods in both daytime and night were also included in this sampling period, and the sampling durations ranged from 2 to 6 hours. Fore fresh SOA, five $PM_{2.5}$ samples from petrol vehicle bench tests conducted under different fuel types and operating conditions were collected. Detailed information about this test system was displayed in Zheng et al. (2017) (Zheng 2017). Two parallel samples were collected and measured under each operating condition to ensure the reliability of the measured data. Two aged SOA samples were collected at the national ambient air background monitoring station in Mount Wuzhi, Hainan Province, from 13-15 April 2015. A complete

secondary transport process was captured during this sampling period, and each sampling duration was 23.5 hours. Lastly, We collected three $PM_{2.5}$ samples representing the biomass combustion source through biomass combustion simulation experiment (He et al., 2010), of which were conducted in the combustion simulation laboratory at Peking University Shenzhen Graduate School on 24-28 May 2017. Pine branches, as a major source of biomass burning in south China (Chen et al., 2017) were selected as the representative plant for the combustion simulation experiment in this study. The pine branches were divided into three weight groups (low (3 kg), medium (6 kg) and high (8 kg)). Samples at three different combustion stages (ignition, flame combustion, and complete combustion) were collected, and the sampling time at each stage was 49, 75, and 90 minutes, respectively. Each sampling and analysis process was repeated three times to ensure reliability.

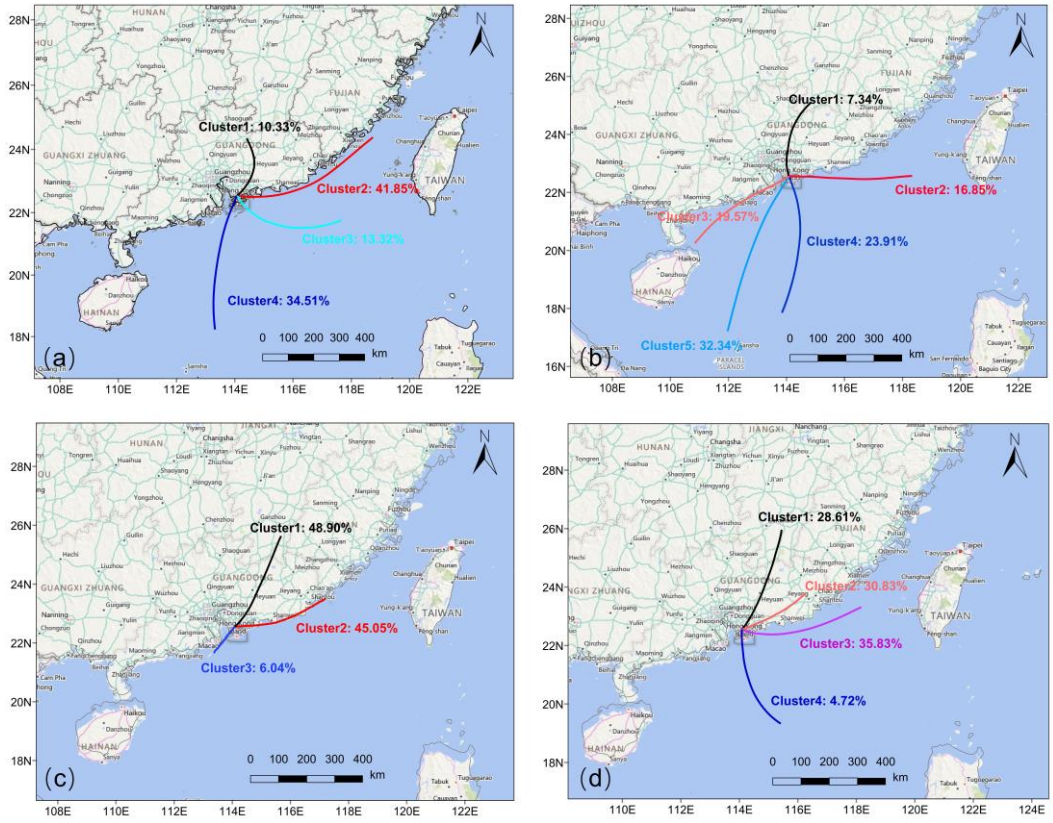
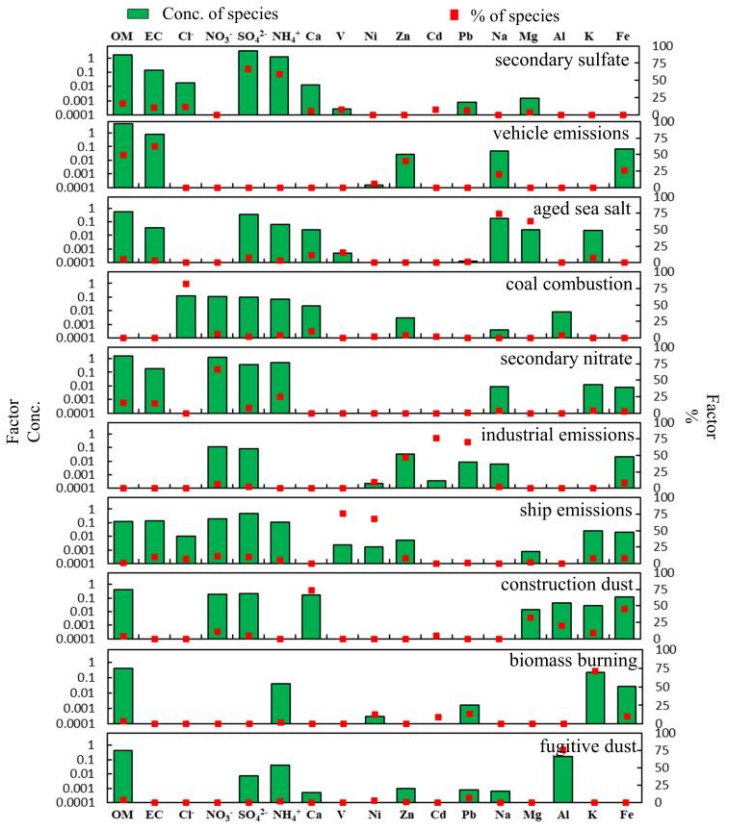


Figure S1. Seasonal backward trajectory of air masses in Shenzhen, 2019. (a) spring (b) summer (c) fall (d) winter. Map image: © Microsoft by MeteoInfoMap.



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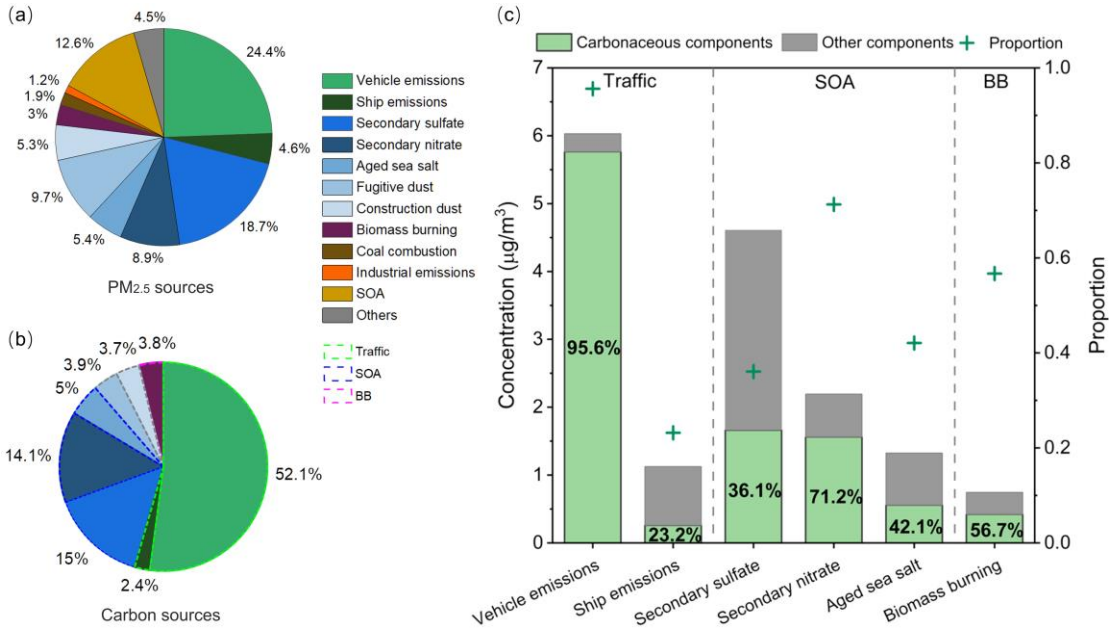
85 **Figure S2.** The source profiles resolved by PMF for $PM_{2.5}$.



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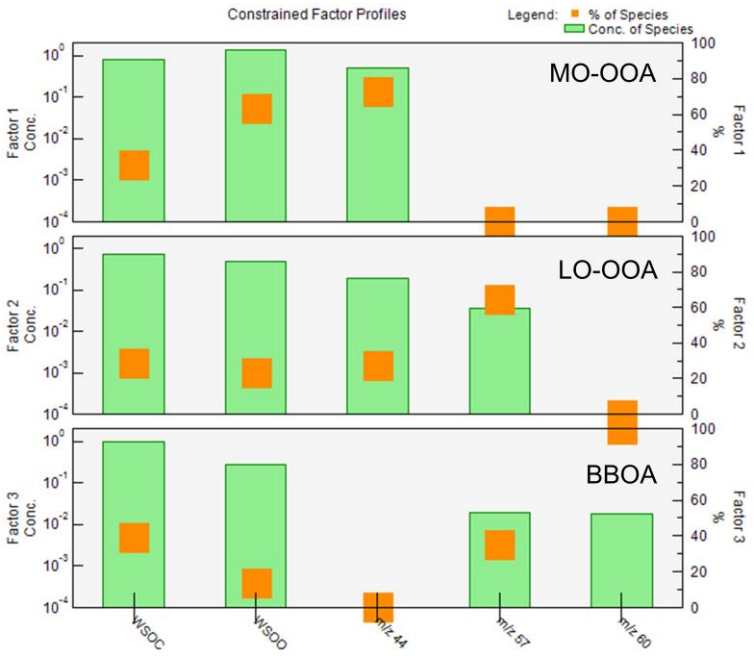
87 **Figure S3.** Source apportionment results of $PM_{2.5}$ (a) and carbonaceous aerosol (b) based on the PMF

88 model. (c) The relative contribution of different sources to $PM_{2.5}$ and carbonaceous fractions.



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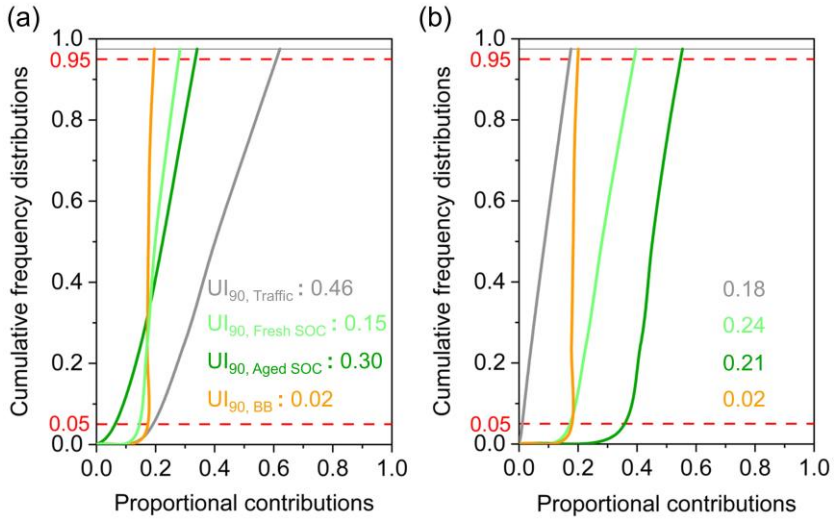
90 **Figure S4.** The source profiles resolved by PMF for WSOC.



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92 **Figure S5.** Cumulative frequency distributions of the proportional contributions from potential sources

93 of TC (a) and WSOC (b) based on BSIM model.

Table S1. Description of the sampling sites in Shenzhen.

Site	Site Code	Coordinates	Site description	
University town	UT	Lat: 22.59°N Long: 113.97°E	Urban	This site reflects the pollution characteristics of typical urban areas and regional transport
Longhua	LH	Lat: 22.68°N Long: 114.01°E	Urban	This site generally reflects the pollution characteristics of urban local emissions
Honghu	HH	Lat: 22.57°N Long: 114.14°E	Urban	This site reflects the pollution characteristics of the general urban areas
Xixiang	XX	Lat: 22.58°N Long: 113.90°E	Urban	This site reflects the pollution characteristics of western industrial urban areas in Shenzhen
Dapeng	DP	Lat: 22.64°N Long: 114.42°E	Background	This site reflects the pollution characteristics of the eastern coastal tourist areas

Table S2. General meteorological conditions during the sampling period in 2019.

	Mean temp. (℃)	Rainfall (mm)	Mean RH (%)	Mean wind speed (m s-1)	Predominant wind direction
Spring (1 Mar-8 Apr)	21.3	151.8	83.0	1.7	ESE
Summer (1 Jun-3 Jul)	28.5	275.8	85.0	2.2	SW
Autumn (1 Sept-11 Oct)	27.6	175.0	74.0	1.6	ESE
Winter (22 Nov-30 Dec)	19.5	3.2	62.0	2.0	NNE

Table S3. Comparison of $\delta^{13}C_{TC}$ source signatures in this study with global datasets.

Emission sources	Continent	Location	Sample types	$\delta^{13}C$(‰)	SD	Ref.
	Asia(This study)	**China, Shenzhen**	**Traffic**	**-26.26**	**0.50**	**-**
	Asia	China	Wucun Tunnel, Entrance	-25.84	0.23	(Yao et al., 2022)
	Asia	China	Wucun Tunnel, Exit	-25.88	0.24	
	Asia	China	Xianyueshan Tunnel, Entrance	-25.88	0.26	
	Asia	China	Xianyueshan Tunnel, Exit	-25.79	0.23	
	Asia	China, Guangzhou	Traffic	-24.6 to -25.5		(Dai et al., 2015)
	Asia	India	Traffic	-25.3	0.3	(Agnihotri et al., 2011)
	Asia	Nepal	Traffic	-26.5 to -26.1		(Shakya;Ziemba and Griffin 2010)
	Asia	China	Traffic	-25.85	0.22	(Yao et al., 2022)
	Asia	China	Traffic	-25.27	0.32	(Chen et al., 2012)
Traffic	Asia	Pearl River Delta	Gasoline exhaust	-28.6	0.6	
	Asia	Pearl River Delta	Diesel exhaust	-27.8	0.2	
	Asia	China	Zhujiang Tunnel, Vehicle emissions	-25	0.3	(Dai et al.,2013)
	Asia	India	Diesel exhaust	-26.3	0.2	
	Asia	India	Bio-diesel exhaust	-26.5	0.1	(Singh et al., 2018)
	Asia	India	Petrol(Gasoline) exhaust	-26.1	0.01	
	North America	Mexico	Tunnel; Diesel vehicle emissions	-24.6	0.3	(López-Veneroni 2009)
	North America	Mexico	Tunnel; Gasoline vehicle emissions	-25.5	0.1	
	Oceania	New Zealand	Mount Victoria Tunnel	-25.9	0.8	(Ancelet et al., 2011)
	Europe	Germany	Gasoline exhaust	–26.2	0.2	(Fisseha et al., 2009)
	Europe	Paris	Diesel exhaust	–26.5	0.5	(Widory et al., 2004)
	Europe	Germany	Diesel exhaust	–27.6	0.01	(Fisseha et al., 2009)
	Europe	Paris	Complete combustion of diesel	-29		(Widory 2006)

	Europe	Paris	Complete combustion of gasoline	-27		(Widory 2006)
	Europe	Paris	Fuel oil exhaust	–26.5	0.5	(Widory et al., 2004)
	Europe	Krakow, Poland	Traffic	-30	1	(Zimnoch et al., 2020)
	worldwide	worldwide	Traffic group1	-26.8	1.1	
	worldwide	worldwide	Traffic group2	-28.9	1.7	(Yao et al., 2022)
	worldwide	worldwide	Traffic group3	30.2	0.9	
SOA	**Asia(Our study)**	**China, Hainan**	**Aged SOC , ambient samples of the Mount Wuzhi**	**-25.54**	**0.28**	**-**
	Asia(Our study)	**China, Shenzhen**	**Fresh SOC , petrol vehicle bench tests**	**-27.31**	**0.73**	
	Europe	Germany	Compounds in SOA: aerosol-phase nopinone	-27.6 to -24.8		
	Europe	Germany	Compounds in SOA: acetone	-35.1 to -38.6		
	Europe	Germany	Compounds in SOA: gas-phase nopinone	-28.8		(Fisseha et al., 2009)
	Europe	Germany	Precursor of SOA: initial β-pinene injected	-30.1		
	Europe	Germany	Precursors of SOA	-29.6	0.2	
	North America	Canada	Secondary particulate organic matter			(Irei et al., 2011)
	North America	Canada,	Secondary particulate organic matter	-32.2 to -32.9		(Irei et al., 2006)
BB	**Asia(Our study)**	**China, Shenzhen**	**Burning experiment results of pine branches**	**-27.58**	**0.24**	**-**
	worldwide	worldwide	C3 plant	-27.2	1.6	
	Asia	China	C3 plant	-27.89	0.26	(Yao et al., 2022)
	Asia	China	Seven C3 plants	-27.12		
	Asia	China	Biomass burning (Seven C3 plants)	-26.99	1.11	
	America	Texas	C3 plant	-27	6	(Boutton 1991)
	Europe	Krakow, Poland	Biomass burning(C3 plants)	-26	2	(Zimnoch et al., 2020)
	Asia	China	C4 smoldering	-14.25		
	Asia	China	C4 flaming	-18.42		
	Asia	China	C4 plant (corn stalk)	-12		(Yao et al., 2022)
	Asia	China	Biomass burning (corn stalk)	-13.09		
	worldwide	worldwide	C4 plant	-13.2	1.1	
	America	Texas	C4 plant	-13	4	(Boutton 1991)

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