Supporting information for:

Fates of secondary organic aerosols in the atmosphere identified from compound-specific dual-carbon isotope analysis of oxalic acid

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1. Supplementary Figure (Figure 1–4)

2. Supplementary Table (Table 1–5)

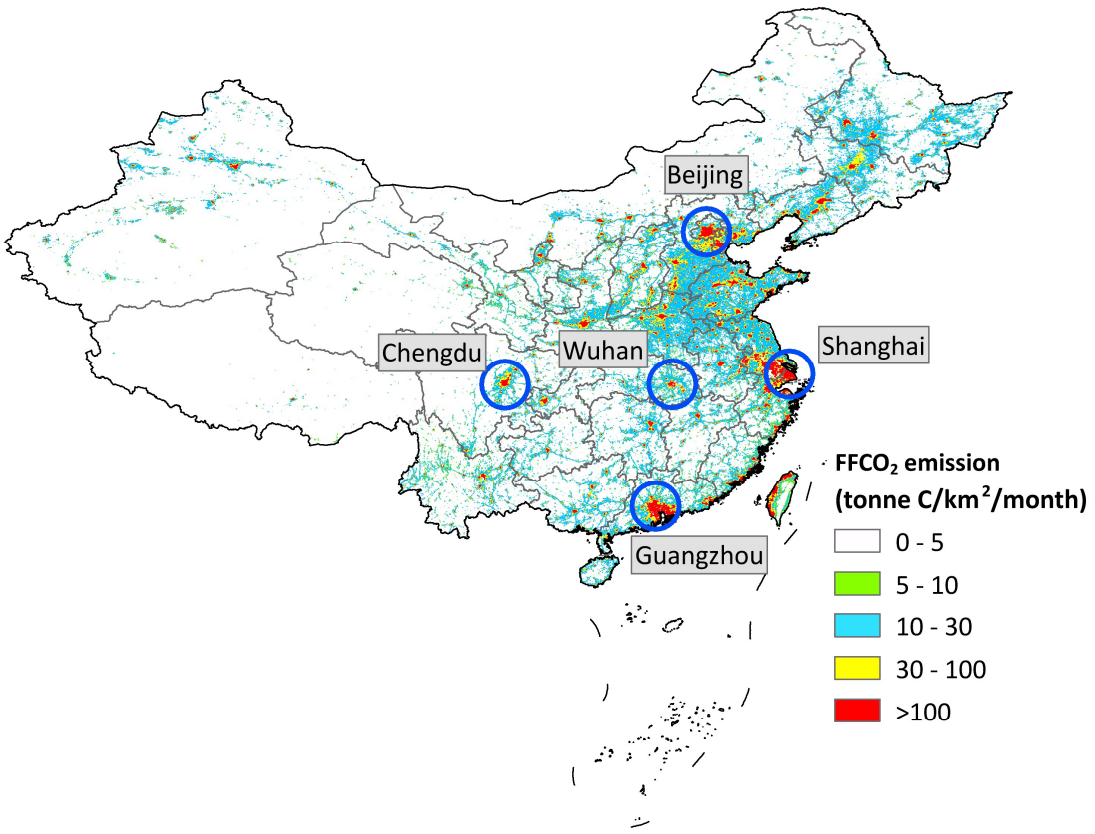

Figure S1. Locations of the five megacities (Beijing, Chengdu, Guangzhou, Shanghai, and Wuhan) and average fossil fuel CO_2 (FF CO_2) emissions during the year 2018. FF CO_2 emissions indicating high levels of anthropogenic activities over the five megacities. The FF CO_2 emission data is obtained from Open-source Data Inventory for Anthropogenic CO_2 (https://db.cger.nies.go.jp/dataset/ODIAC/DL_odiac2020b.html). The administration boundaries in the map are originated from map products of National Geomatics Center of China (https://www.webmap.cn/).

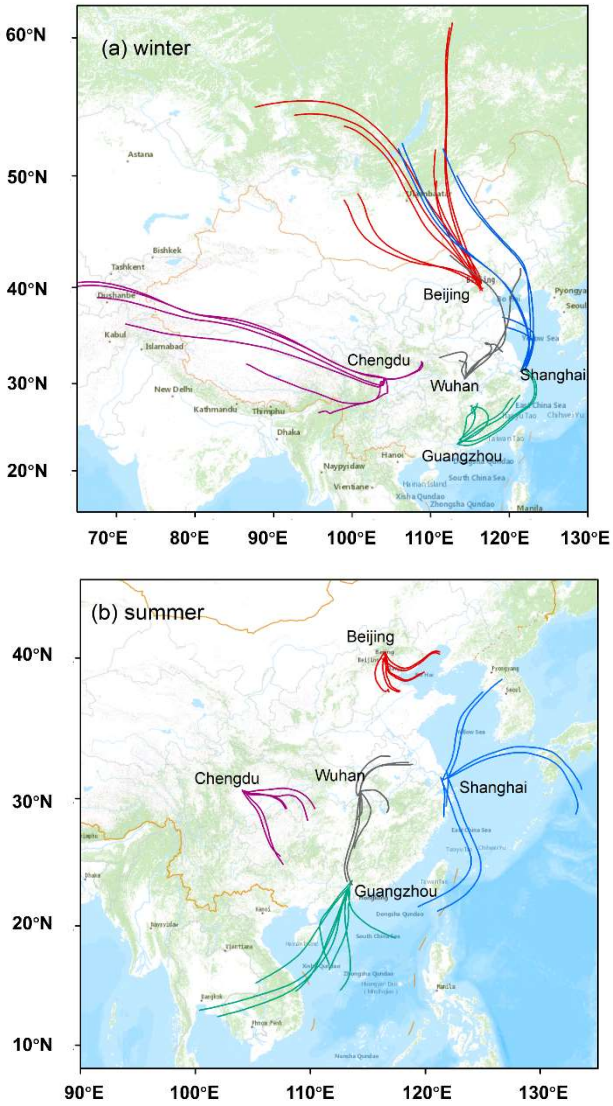

Figure S2. Cluster analysis of 3-day air mass backward trajectories computed at an altitude of 100 m for the sampling sites in Beijing, Shanghai, Guangzhou, Wuhan, and Chengdu during January 2018 (a) and July 2018 (b). The maps are originated from ArcGIS hub free map data (https://hub.arcgis.com/maps/0c539fdb47d34b17bd1452f6b9f49e97/explore?location=17.762116%2C-74.005269%2C3.65).

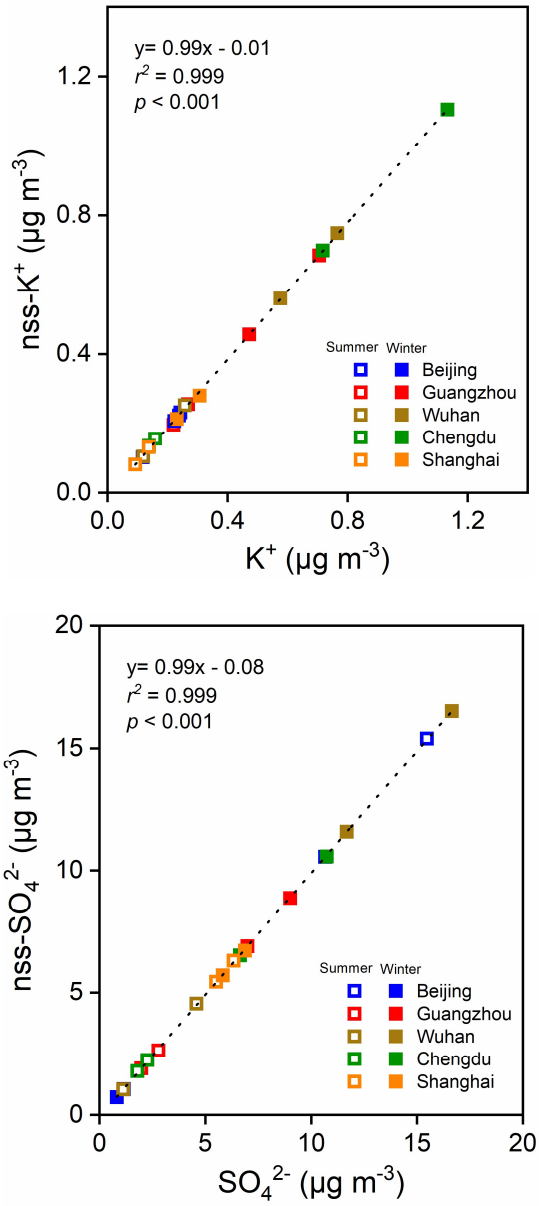

Figure S3. Ratios of non-sea-salt potassium (nss-K^+) to total K^+ and non-sea-salt sulfate (nss-SO_4^{2-}) to total SO_4^{2-}.

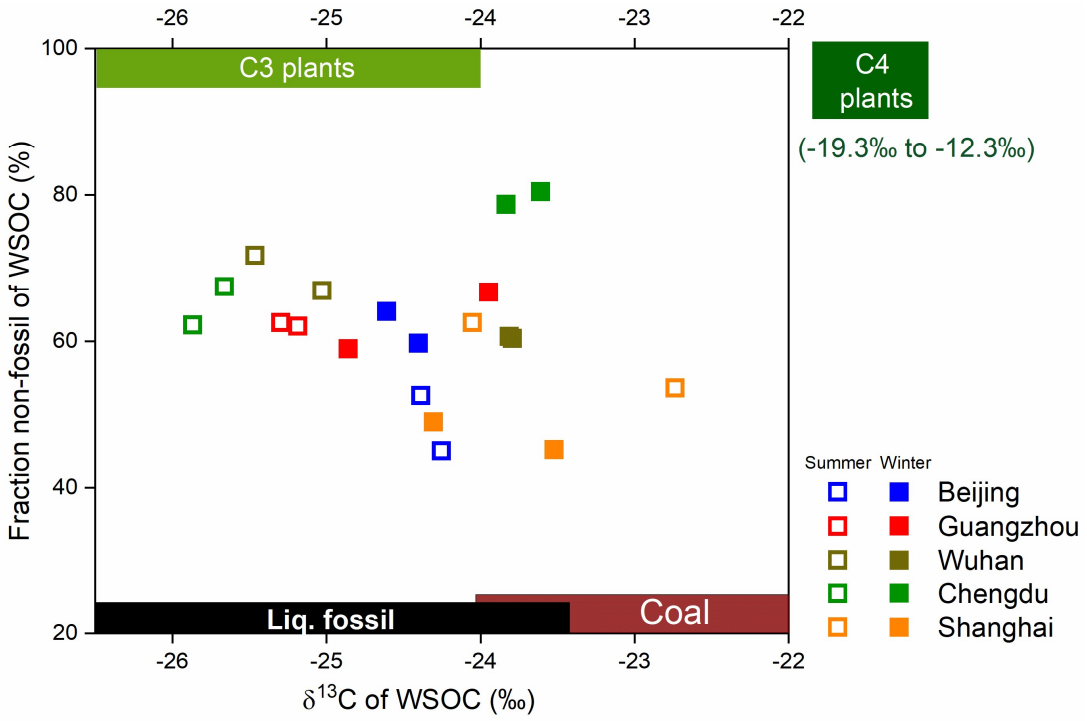

Figure S4. ^{14}C-based non-fossil source fractions plotted against the $\delta^{13}C$ values for water-soluble organic carbon (WSOC) in $PM_{2.5}$ collected in Beijing (blue), Guangzhou (red), Wuhan (brown), Chengdu (green), and Shanghai (orange) in summer (open squares) and winter (filled squares).

Table S1. Information on sampling sites and deployment periods.

City	Site attribution	Location	Cycle starts in winter	Cycle ends in winter	Cycle starts in summer	Cycle ends in summer
Beijing	Urban	39.974°N, 116.370°E	2018/1/5	2018/1/12	2018/7/28	2018/8/3
	Suburban	40.408°N, 116.674°E	2018/1/5	2018/1/12	2018/7/28	2018/8/3
Shanghai	Urban	31.316°N, 121.423°E	2018/1/19	2018/1/25	2018/7/28	2018/8/3
	Suburban	31.524°N, 121.959°E	2018/1/18	2018/1/24	2018/7/28	2018/8/3
Guangzhou	Urban	23.149°N, 113.358°E	2018/1/18	2018/1/24	2018/6/29	2018/7/5
	Suburban	23.650°N, 113.624°E	2018/1/18	2018/1/24	2018/6/29	2018/7/5
Wuhan	Urban	30.531°N, 114.308°E	2018/1/19	2018/1/25	2018/7/28	2018/8/3
	Suburban	30.531°N, 114.332°E	2018/1/18	2018/1/24	2018/7/28	2018/8/3
Chengdu	Urban	30.629°N, 104.064°E	2018/1/18	2018/1/24	2018/7/28	2018/8/3
	Suburban	30.563°N, 104.272°E	2018/1/18	2018/1/24	2018/7/28	2018/8/3

Table S2. Mass concentration of dicarboxylic acids, oxocarboxylic acids, and α-dicarbonyls in $PM_{2.5}$ samples from the five hot spot emission locations of China.

	Summer (N = 10)		Winter (N = 10)	
	Range	Mean/SD	Range	Mean/SD
I. Dicarboxylic Acids, ng m^{-3}				
Oxalic, C_2	59.2-713.3	412.8±201.5	19.2-1077.9	740.1±324.4
Malonic, C_3	3.1-44.7	30.5±12.2	0.8-53	26.8±16
Succinic, C_4	3.1-44.5	25.4±11.9	1.6-66	39.5±21.3
Glutaric, C_5	0.6-9.7	4.9±2.7	0.3-18.9	10.7±6
Adipic, C_6	0.5-5	2.9±1.5	0.2-8.7	4.8±2.5
Pimelic, C_7	0.2-2.5	1.3±0.8	0-5.2	2.3±1.5
Suberic, C_8	0.4-5.2	2.6±1.6	0.1-7.7	3.2±2.2
Azelaic, C_9	0.7-31.3	11.4±9	0.3-21.4	8.6±6.2
Sebacic, C_{10}	0.1-1.6	0.8±0.4	0-3.3	1.3±1.1
Undecanedioic, C_{11}	0.1-1.9	0.6±0.5	0-1.9	0.7±0.6
Dodecanedioic, C_{12}	0-0.4	0.2±0.1	0-0.7	0.3±0.2
Methylmalonic, iC_4	0.1-0.9	0.7±0.3	0-1.1	0.6±0.3
Methylsuccinic, iC_5	0.3-2.7	1.8±0.8	0.3-7.1	4.1±2.5
2-Methylglutaric, iC_6	0.1-0.9	0.5±0.3	0.1-1.7	1±0.6
Maleic, M	0.2-3.8	1.5±1	0.1-4.1	2±1.2
Fumaric, F	0.2-1.7	1±0.4	0.1-1.5	0.8±0.4
Methylmaleic, Mm	0.4-4	2.9±1.2	0.3-7.6	3.7±2
Phthalic, Ph	2.1-25.4	10.2±7.1	1.3-17.7	6±5
Isophthalic, iph	0-0.4	0.2±0.1	0-0.7	0.2±0.2
Terephthalic, tPh	0.6-11.2	5.7±4	0.4-18.1	6.6±5.6
4-Ketopimelic, kC_7	0.2-8.5	4±2.6	0-6.7	1.9±2
Total diacids	75.5-871	521.8±233.8	25.4-1269.2	865.2±384.5
II. Oxocarboxylic Acids, ng m^{-3}				
Pyruvic, Pyr	0.4-10	6.4±2.8	0.2-23.4	9.3±7.3
Glyoxylic, ωC_2	2.5-27.1	18.2±7.4	2.1-69.3	41.1±20.8
3-Oxopropanoic, ωC_3	0.5-5.1	3.4±1.4	0.4-2.7	1.6±0.7
4-Oxobutaboic, ωC_4	0.5-5.6	3.6±1.6	0.4-4.4	2.1±1.1
5-Oxopentanoic, ωC_5	0-11.9	1.9±3.8	0-29.7	14.9±10.6
6-Oxoheptanoic, ωC_6	0-4.6	2.5±1.4	0-5.5	3.1±1.9
Total oxoacids	3.9-55.9	36±15.1	3.1-113.1	72±37.9
III. α-Dicarbonyls, ng m^{-3}				
Glyoxal, Gly	0.1-15.2	3.7±5	0.1-27	7.7±8.4
Methylglyoxal, mGly	11.2-72.2	33.3±20.8	12.2-89.7	56.6±28.7
Total dicarbonyls	11.2-87.4	37±25.5	12.3-111.1	64.3±35.8

Table S3. The mass concentration, stable carbon composition ($\delta^{13}C$, ‰), and ^{14}C-based source apportionment (fraction of non-fossil; f_{NF}) of oxalic acid in the $PM_{2.5}$ samples from the five hot spot emission locations of China.

City	Season	Site attribute	Concentration (ng m^{-3})	$\delta^{13}C$ (‰)	f_{NF} (%)
Guangzhou	Summer	Suburban	491.3	-22.8±0.5	75.7±1.7
		Urban	502.0	-23.2±0.2	72.7±2.4
	Winter	Suburban	888.4	-26.7±0.6	63.6±1.2
		Urban	571.2	-27.5±0.4	63.7±1.5
Beijing	Summer	Suburban	705.0	-22±1.0	57.5±1.4
		Urban	713.3	-23.7±0.1	43.5±1.3
	Winter	Suburban	19.2	-22±1.1	nd
		Urban	424.5	-29.7±1.4	44.1±4.9
Wuhan	Summer	Suburban	59.2	-22.3±0.1	nd
		Urban	302.1	-22.6±0.2	73.1±4.4
	Winter	Suburban	732.4	-27±0.4	64.6±1.4
		Urban	1077.9	-27.2±0.6	59.6±1.4
Chengdu	Summer	Suburban	262.7	-23.5±0.6	71.4±5.0
		Urban	316.8	-25.1±0.9	62.8±4.5
	Winter	Suburban	1038.6	-26.9±0.7	63.1±1.3
		Urban	972.1	-26.6±1.2	59.3±1.0
Shanghai	Summer	Suburban	335.5	-14.1±0.1	66±1.8
		Urban	439.6	-18.6±0.2	71.6±1.6
	Winter	Suburban	817.0	-23.7±0.1	41.5±0.5
		Urban	859.5	-24.7±1.0	39.6±1.2

[a] nd: non data

Table S4. Compound-specific stable carbon isotope ratios ($\delta^{13}C$, ‰) of dicarboxylic acid and oxocarboxylic acid in $PM_{2.5}$ samples from the five hot spot emission locations of China.

	Summer (N = 10)		Winter (N=10)	
	Range	Mean/SD	Range	Mean/SD
I. Dicarboxylic Acids				
Oxalic, C_2	-25.1 to -14.1	-21.8±3.2	-29.7 to -22.0	-26.2±2.2
Malonic, C_3	-24.9 to -18.4	-21.7±1.8	-26.7 to -20.7	-23.2±2.1
Succinic, C_4	-28.6 to -20.7	-24.4±2.1	-27.6 to -23.0	-24.2±1.5
Azelaic, C_9	-29.8 to -26.7	-28.1±0.8	-32.5 to -26.2	-29±1.7
Phthalic, Ph	-31.7 to -27.8	-29.4±1.3	-37.1 to -26.0	-30.5±3.5
II. Oxocarboxylic Acid				
Glyoxylic, ωC2	-39.8 to -19.3	-32.5±5.4	-45.9 to -30.1	-37.2±4.9

Table S5. The concentrations of major chemical components in $PM_{2.5}$ samples from the five hot spot emission locations of China.

	Summer (N = 10)		Winter (N = 10)	
	Range	Mean/SD	Range	Mean/SD
$PM_{2.5}$, μg m^{-3}	32.2-163.7	80.5±44.3	2.4-137.8	92.2±44.7
WSOC, μg m-3	1.1-3.8	2.2±0.8	1.1-9.6	4.1±2.5
NO_3^-, μg m^{-3}	0.9-7.9	3.2±2.5	1.4-62.7	26.3±20.1
nss-SO_4^{2-}, μg m^{-3}	1.1-15.5	5.3±4.6	0.8-16.6	7.6±4.7
NH_4^+, μg m^{-3}	0.5-8.2	3.0±2.8	0.7-16.9	7.6±5.2
nss-K^+, μg m^{-3}	0.1-0.3	0.2±0.1	0.1-1.1	0.5±0.3
$WSIC_{anth}$[a], μg m^{-3}	2.5-31.5	11.7±9.6	3.5-100.4	43.5±30.9
ALWC[b], μg m^{-3}	2.6-19.4	8.5±5.1	1.4-229.8	59.7±76.1

[a] anthropogenic water-soluble inorganic constituents ($WSIC_{anth}$) = non-sea-salt (nss) K^+ + nss-SO_4^{2-} + NH_4^+ + NO_3^- + nss-Cl^- [b] aerosol liquid water content