



## Seasonal Variations and Sources of Carboxylic Acids in PM<sub>2.5</sub> in Wuhan, China

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### ABSTRACT

Aerosol PM<sub>2.5</sub> samples collected from three sites in Wuhan, China, during 2011–2012 were analyzed by gas chromatography-mass spectrometry to better understand the molecular composition and sources of carboxylic acids. The concentrations of total monocarboxylic acids did not show apparent seasonal variations in Wuhan. Palmitic acid and stearic acid were the most abundant species, accounting for 32.4%–62.4% (average 51.8%) of all quantified monocarboxylic acids. Oxalic acid was found as the most dominant dicarboxylic acid, followed by succinic acid at the three sampling sites. The total concentration of dicarboxylic acids displayed obvious seasonal variation, with the highest in summer (1036.7–1546.4 ng/m<sup>3</sup>) and the lowest in winter (126.8–211.0 ng/m<sup>3</sup>). Positive matrix factorization (PMF) revealed that coal combustion, traffic-related emissions and biomass burning are the most important contributors to carboxylic acids at industrial site, downtown site and botanical garden, respectively. Plant waxes and secondary photochemical products are also significant sources of carboxylic acids at the three sampling sites.

**Keywords:** Organic aerosols; Monocarboxylic acids; Dicarboxylic acids; Positive matrix factorization; Photochemical products.

### INTRODUCTION

Organic acids, containing monocarboxylic acids, dicarboxylic acids, aromatic acids and hydroxyl acid, have been reported as the dominant constituents of organic matter in the atmosphere. Organic acids typically accounted for about 30%–70% of solvent extractable organic compounds in many cities (Yue *et al.*, 2004; He *et al.*, 2006) and they have received much attention because of their hygroscopic features and capability of acting as cloud condensation nuclei (CCN) (Novakov and Penner, 1993). Carboxylic acids have been found in the urban, rural, and marine atmosphere (Kawamura and Ikushima, 1993; Kawamura *et al.*, 1996a; Kerminen *et al.*, 2000; Yao *et al.*, 2002; Huang *et al.*, 2005; Ho *et al.*, 2006). The previous studies demonstrate that carboxylic acids can significantly contribute to the acidity of rainwater in urban and rural environments (Kawamura *et al.*, 1996b). They have potential to alter the hygroscopic property of atmospheric aerosols and hence to change global radiation balance as well as causing health problems (Facchini *et al.*,

1999; Kerminen, 2001). Organic acids have several different sources, including the primary emissions from vehicle emission, meat cooking, fossil fuel combustion and biomass burning, homogeneous photochemical oxidation of organic precursors from both anthropogenic and biogenic origins (Simoneit, 1984; Kawamura and Gagosian, 1987; Kawamura and Kaplan, 1987; Simoneit, 1989; Rogge *et al.*, 1991, 1993a; Schauer *et al.*, 1999b). So far, possible pathways from some gas-phase and primary precursor to carboxylic acids were also proposed but limited (Kawamura *et al.*, 1996b; Yao *et al.*, 2002, 2004).

Measurements of atmospheric carboxylic acids in China, mainly in megacities such as Beijing, Shanghai, Nanjing, Guangzhou, Xi'an and Hongkong, have been reported (Wang *et al.*, 2002; Cao *et al.*, 2003; Huang *et al.*, 2005; Zheng *et al.*, 2005; Feng *et al.*, 2006; He *et al.*, 2006; Wang *et al.*, 2006; Ho *et al.*, 2007; Wang *et al.*, 2012). However, little is known about carboxylic acids in Wuhan aerosol. Wuhan is the most populous city in Central China with an area of 8494 km<sup>2</sup> and a population of ten millions. Previous studies about atmospheric particulate matter in Wuhan were reported and most of them focused on the concentration level and element component of PM<sub>10</sub> and PM<sub>2.5</sub> (Feng *et al.*, 2011). In this paper, we tried to measure the molecular compositions of carboxylic acids, including monocarboxylic acids and dicarboxylic acids, in aerosol PM<sub>2.5</sub> collected in Wuhan, provide insight into

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seasonal and spatial variations of these species, and investigate their sources and formation mechanisms by using PMF model and mixing ratios of individual compounds.

## METHOD

### Sample Site and Collecting

Aerosol PM<sub>2.5</sub> samples were collected at three sites of Wuhan (Fig. 1) during 2011–2012 using a middle-volume sampler (Qingdao Laoshan Electronic instrument, 100 L/min) on prebaked (450°C, 8 hours) quartz fiber filter (Pallflex,  $\Phi = 9$  cm). The sampling periods were from 10 October to 23 October 2011, 2 January to 15 January 2012, 2 April to 15 April 2012 and 2 July to 15 July 2012, which represents fall, winter, spring and summer respectively. Three sample sites were chosen at Industry Area (Qingshan), Downtown Area (Xiongchu Avenue) and Botanical Garden (East Lake). Therefore, we named these three sites as ID, DT and BG, respectively. PM<sub>2.5</sub> samples were simultaneously collected from 9:00 a.m. to 7:00 p.m. at each site. After sampling, the filters were dried in a desiccator for 24 h and weighed. Then the loaded filters were wrapped separately in aluminium foil and stored in a refrigerator at  $-18^{\circ}\text{C}$  until extraction.

### Organic Acids Analysis

A half of each aerosol filters were cut into small pieces and extracted with two 20 mL aliquots of dichloromethane (Spectrum pure, Fisher) and two 20 mL of methanol (ACROS) for ten minutes each in a sonicator. The combined extract was concentrated using a vacuum rotary evaporator to about 5 mL. The solvent extracts were filtered using a PTFE filtration unit to an annealed glass tube for the removal of insoluble particles (Simoneit and Mazurek, 1982), and then transferred into a conical vial to blow dry under a gentle stream of pre-purified nitrogen gas. Then, we dissolved the extracts using 250  $\mu\text{L}$  n-hexane (Spectrum pure, Fisher).

A half of extracts were transferred into a conical vial accurately by pipette (Across Plus, 250  $\mu\text{L}$ ) and derivatized with BSTFA/TMCS 99:1 (Regis Technologies, Inc. USA) in sealed vials at  $70^{\circ}\text{C}$  for 2 h and then analyzed by gas chromatography-mass spectrometry (GC: Agilent 6890, MS: Agilent 5973) (Schummer *et al.*, 2009; Pietrogrande *et*

*al.*, 2010). Due to the extract solvents and BSTFA/TMCS derivatization in our sample pretreatment, oxalic acid can not be accurately quantified (Kawamura and Ikushima, 1993; Pietrogrande *et al.*, 2010). Therefore, oxalic acid were quantified from another quarter aerosol filters by our group. Briefly, one quarter of the filter was extracted with pure water (10 mL, 3 times), which was made by oxidizing organic impurities of Milli Q water with UV light. The extracts (water soluble organics) were passed through a glass column (Pasteur pipette) packed with a quartz wool to remove particles such as filter debris and then concentrated to ca. 0.1 mL using a rotary evaporator under a vacuum. They were further dried by nitrogen blow down and reacted with 14% BF<sub>3</sub>/n-butanol at  $100^{\circ}\text{C}$  to derive the carboxyl groups to butyl esters and the aldehyde groups to dibutoxyacetals. The derivatives were extracted with n-hexane after adding pure water and then determined with GC-MS.

GC-MS using an Agilent Model 5973 MSD operated in the electron impact mode at 70 eV and coupled to an Agilent Model 6890 gas chromatograph. GC-MS fitted with a fused silica capillary column (DB-5, 30 m, 0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness). The oven temperature was maintained at  $60^{\circ}\text{C}$  for 5 min and then programmed to increase at  $5^{\circ}\text{C}/\text{min}$  to  $300^{\circ}\text{C}$ , at which temperature it was then held for 30 min. Helium (99.999% purity) was used as the carrier gas at a flow rate of 1.0 mL/min.

GC-MS data were acquired and processed with an Agilent Chemstation. Individual organic acid compounds were identified by GC retention times, mass spectra, and comparison with authentic standards. Field blanks, filter blanks and solvent blanks were also determined. No significant field blanks and solvent blanks of any species were detected. Duplicate analyses of 6 filter samples showed that analytical errors are within 10% for most of the species. Recoveries of authentic standards were found for all the target compounds ranging from 80% (docosanoic acid) to 112% (succinic acid). More details were shown in Table 1. To better identify the sources of carboxylic acids, we add some major tracers (levoglucosan, cholesterol, phthalic acid) into the PMF model. These organic compounds were measured following BSTFA derivatization of the aerosol extract and GC-MS analysis.

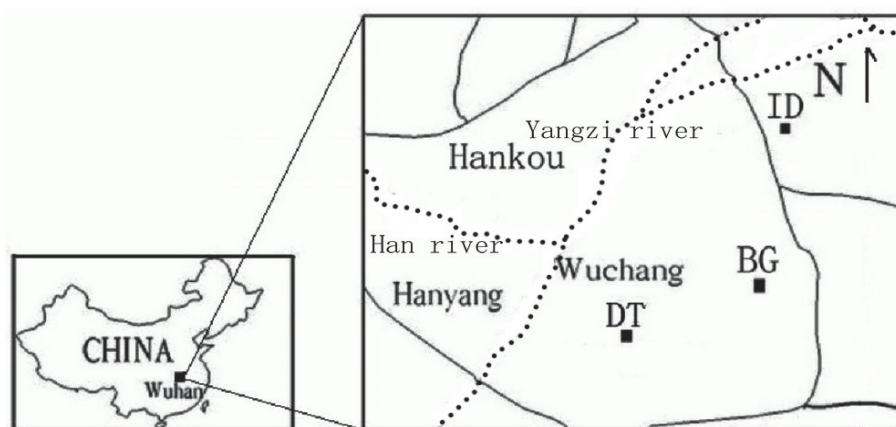


Fig. 1. Locations of three sampling sites in Wuhan, China.

**Table 1.** Analytical parameters for calibration and method evaluation.

Species	Correlation (R <sup>2</sup> )	(SD% n = 6)		MDL (ng/m <sup>3</sup> )	Recoveries (%)
		Samples	Standard Material		
C <sub>11</sub>	0.9802	10.25	7.32	0.41	83.21
C <sub>12</sub>	0.9773	11.78	8.81	0.32	87.64
C <sub>13</sub>	0.9835	13.95	5.65	0.14	85.34
C <sub>14</sub>	0.9846	10.27	9.84	0.17	90.01
C <sub>15</sub>	0.9931	6.79	10.32	0.19	87.38
C <sub>16</sub>	0.9978	12.35	4.33	0.22	92.37
C <sub>17</sub>	0.9734	7.89	11.06	0.36	89.65
C <sub>18:0</sub>	0.9914	12.43	11.65	0.11	90.39
C <sub>18:1</sub>	0.9765	14.78	12.03	0.31	87.66
C <sub>18:2</sub>	0.9639	11.08	11.98	0.22	82.35
C <sub>19</sub>	0.9825	7.89	8.96	0.17	89.79
C <sub>20</sub>	0.9804	13.77	5.75	0.32	91.67
C <sub>21</sub>	0.9659	12.34	6.62	0.19	83.73
C <sub>22</sub>	0.9792	10.85	10.91	0.25	80.00
C <sub>23</sub>	0.9701	11.87	6.43	0.33	85.39
C <sub>24</sub>	0.9809	5.98	7.57	0.20	93.24
C <sub>25</sub>	0.9700	8.39	6.67	0.35	82.77
C <sub>26</sub>	0.9731	12.07	7.12	0.19	87.75
C <sub>27</sub>	0.9640	14.32	8.89	0.14	79.63
C <sub>28</sub>	0.9670	11.32	14.79	0.38	82.37
C <sub>29</sub>	0.9734	7.97	8.43	0.23	85.81
C <sub>30</sub>	0.9731	14.68	11.87	0.15	89.56
C <sub>31</sub>	0.9691	9.87	11.80	0.12	82.39
C <sub>32</sub>	0.9701	12.60	9.41	0.31	84.22
di-C <sub>3</sub>	0.9874	12.02	8.49	0.25	80.36
di-C <sub>4</sub>	0.9902	7.33	11.94	0.18	112.54
di-C <sub>5</sub>	0.9851	12.56	11.38	0.23	86.78
di-C <sub>6</sub>	0.9731	9.55	13.64	0.44	94.57
di-C <sub>7</sub>	0.9835	10.79	11.58	0.31	91.05
di-C <sub>8</sub>	0.9615	7.79	9.84	0.18	80.30
di-C <sub>9</sub>	0.9875	13.80	8.70	0.22	84.78
di-C <sub>10</sub>	0.9805	9.76	12.79	0.28	82.57
Ph	0.9871	5.67	8.10	0.54	89.36

## RESULTS AND DISCUSSION

### Monocarboxylic Acids

The homologous series of C<sub>11</sub>–C<sub>32</sub> monocarboxylic acids (MCAs) in PM<sub>2.5</sub> samples were detected. As shown in Fig. 2, the palmitic acid is the most abundant species followed by stearic acid at all three sampling sites over the year studied. The total concentration of monocarboxylic acids ranged from 56.11–809.01 ng/m<sup>3</sup>, 42.06–435.84 ng/m<sup>3</sup> and 34.25–371.92 ng/m<sup>3</sup> at ID, DT and BG sampling site, respectively. The concentrations of monocarboxylic acids did not show apparent seasonal variations at three sampling sites. Compared to other megacities in China (Table 2), the concentration of monocarboxylic acids in Wuhan was less than Beijing and Guangzhou. Monocarboxylic acids are derived from direct vegetation emission and human activities such as combustion of fossil fuel and biomass, paved road dusts (Rogge *et al.*, 1993b) and cooking operations (Rogge *et al.*, 1991; Schauer *et al.*, 1999a; He *et al.*, 2004). The lower concentration in Wuhan may suggest primary pollutions

especially anthropogenic pollutions were not serious than Beijing and Guangzhou.

It is worthy to note that oleic acid and linoleic acid were detected in aerosol samples. The ratio of oleic acid to stearic acid (C<sub>18:1</sub>/C<sub>18:0</sub>) is often used as an indication of the aging of the aerosols (Kawamura and Gagosian, 1987; Simoneit and Mazurek, 1982). The more aged aerosol often show lower ratio of C<sub>18:1</sub>/C<sub>18:0</sub>. The seasonal average ratios of oleic acid to stearic acid in Wuhan aerosol were shown in Fig. 3. The ratios in Wuhan (0.15, 0.08, 0.09, 0.22 in spring, summer, fall and winter, respectively) were much lower than Beijing (0.29, 0.48 in fall and winter, respectively), Qingdao (0.68, 0.32, 0.88, 0.60 spring, summer, fall and winter, respectively) and Hong Kong (1.93, 0.69 in summer, and winter, respectively) except summer in Beijing (0.04) (Guo *et al.*, 2003; He *et al.*, 2006; Zheng *et al.*, 2000). The aerosols at DT and BG sites in Wuhan were more aged in summer. The low ratio in summer may be due to the high temperature, humidity, frequent reactions of radicals, ozone and other oxidants (Simoneit *et al.*, 1988; Zheng *et al.*, 2000).

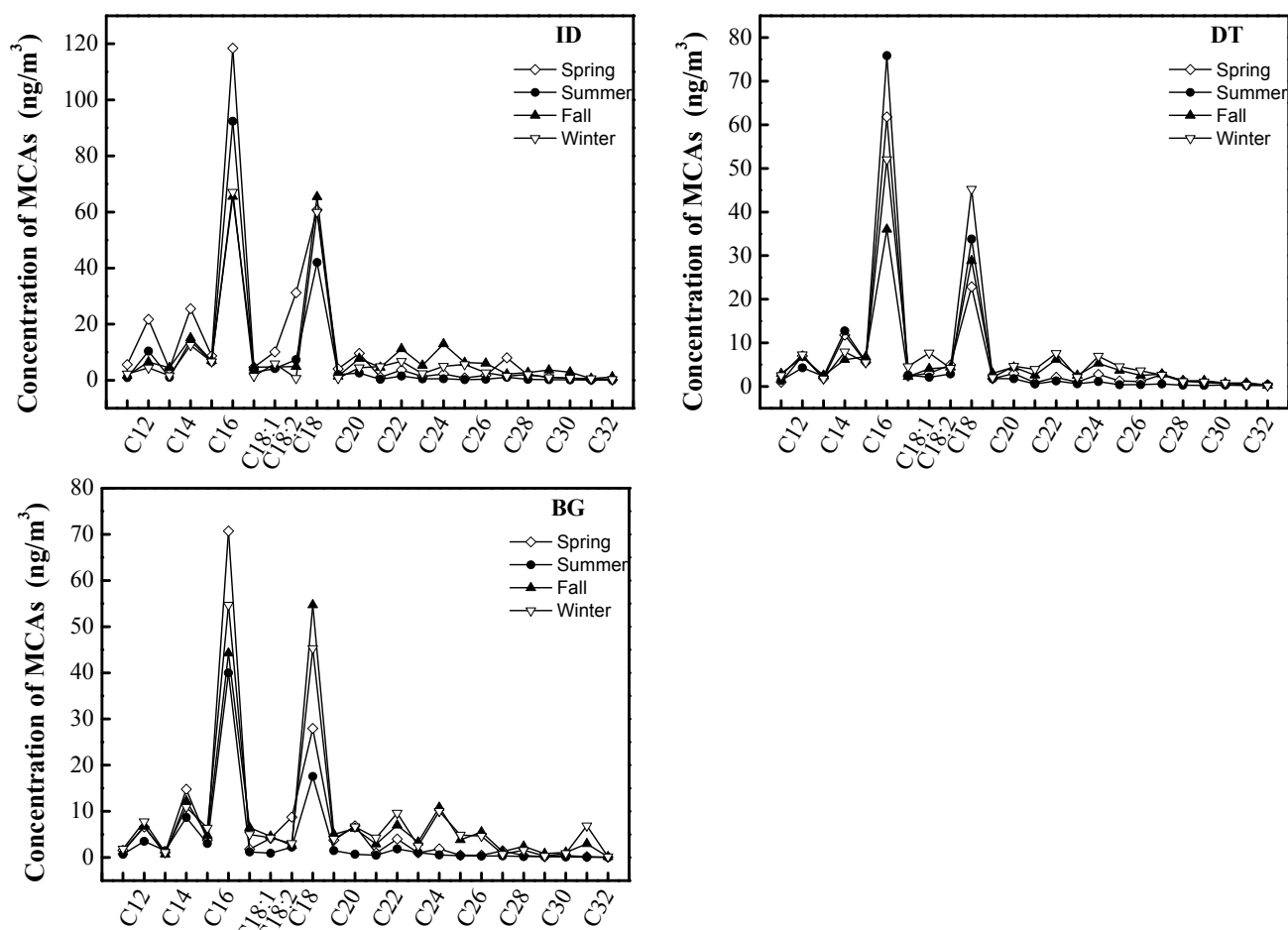


Fig. 2. Typical seasonal average distribution diagrams of monocarboxylic acids.

Table 2. Comparison of concentrations of carboxylic acids in aerosols in some cities of China (ng/m<sup>3</sup>).

Site	Period	Size	MCAs	DCAs	References
Beijing	2002–2003	PM <sub>2.5</sub>	383.3	342.7 <sup>a</sup>	Huang <i>et al.</i> , 2005; He <i>et al.</i> , 2006
Qingdao	2001.6–2002.5	TSP	653.6		Guo <i>et al.</i> , 2003
Guangzhou	2006.7–2007.4	TSP	630.6	3704	Ma <i>et al.</i> , 2010
Nanjing	2001.2–2001.5	PM <sub>2.5</sub>		1319.5	Wang <i>et al.</i> , 2002
Wuhan	2011.10–2012.7	PM <sub>2.5</sub>	191.0	755.4	This work

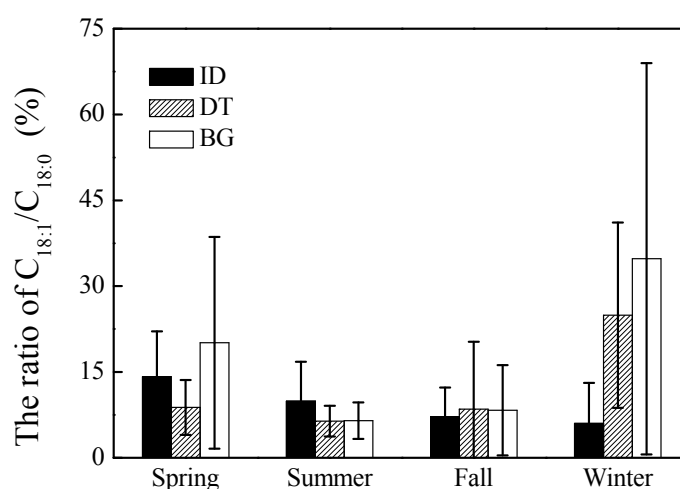
<sup>a</sup> di-C<sub>2</sub>–di-C<sub>4</sub> were quantified by Huang and di-C<sub>5</sub>–di-C<sub>10</sub> were quantified by He *et al.*, 2006.

The dominance of even carbon number acids to odd carbon number acid isomers is determined by carbon preference index (CPI) and is calculated as

$$\text{Acid CPI} = \frac{\sum \text{Even carbon number acids}}{\sum \text{Odd carbon number acids}} \quad (1)$$

High CPI generally indicates biogenic origins. CPI values at three sites were calculated based on the C<sub>11</sub>–C<sub>32</sub> homologues, which varied from 1.1 to 17.9, 1.2 to 13.3, and 1.0 to 11.5 at ID, DT and BG sites respectively. As shown in Table 3, the CPI value displayed highest in summer, implying enhanced emissions from biogenic origins of aerosols such as plant wax particles (Simoneit, 1984; Guo *et al.*, 2003).

The < C<sub>20</sub> homologues are thought to be derived in part from microbial sources, while > C<sub>22</sub> homologues, especially C<sub>26</sub>–C<sub>30</sub> are from vascular plant wax (Simoneit and Mazurek, 1982; Rogge *et al.*, 1993c). Besides microbial activities, food cooking has also been found to be an important contributor of monocarboxylic acids in urban areas (Rogge *et al.*, 1991; Schauer *et al.*, 1999a; He *et al.*, 2004). Meanwhile, vehicles emissions and cigarette also have certain influence on monocarboxylic acids (Rogge *et al.*, 1994; Schauer *et al.*, 1999b; He *et al.*, 2004). In Table 3, the ratios of < C<sub>20</sub> homologues to > C<sub>22</sub> homologues were 3.6–39.2 for three sites in different seasons. The ratios in summer at three sites were approximately 2 times higher than spring and 3 times higher than fall and winter, implying enhanced microbial sources and meat cooking such as barbecue in summer.



**Fig. 3.** Seasonal average ratio of oleic acid to stearic acid.

**Table 3.** The characteristic parameters of monocarboxylic acids.

	CPI			$C_{\leq 20}/C_{>22}$		
	ID	DT	BG	ID	DT	BG
Spring	7.77	7.16	5.32	17.46	13.63	13.55
Summer	10.39	8.04	7.63	39.17	28.61	25.32
Fall	5.51	4.20	4.90	5.76	4.83	4.29
Winter	5.51	3.55	3.52	5.36	4.62	3.61

Actually, open air barbecue is a very popular activity in Wuhan especially during summer evening. It is noteworthy that higher plant wax content in total monocarboxylic acids is normally higher in winter than that in summer (Guo *et al.*, 2003). The fatty acid wax content in dead leaves during wintertime is approximately 5 times higher than that in green leaves (Rogge *et al.*, 1993c). The ratios of  $C_{26}$ – $C_{30}$  monocarboxylic acids to all quantified monocarboxylic acids in fall (average 6.8%) and winter (average 7.2%) were much higher than spring (average 3.2%) and summer (average 1.0%) at three sites. Therefore, the lowest ratios in fall and winter were probably due to the wind abrasion of dead leaves which contain relative abundant high molecular weight (HMW) monocarboxylic acids (Simoneit, 1986).

#### Dicarboxylic Acids

The average seasonal concentration of dicarboxylic acid (di- $C_2$ –di- $C_{10}$ ) in aerosol  $PM_{2.5}$  at three sites was summarized in Table 4. Total dicarboxylic acids concentration ranged from 126.79  $ng/m^3$  to 1546.4  $ng/m^3$  with the average of 755.4  $ng/m^3$ . The concentrations of dicarboxylic acid in summer were approximately 3 times higher than fall and 9 times higher than winter. Kawamura and Ikushima (1993) reported that diacids are present at higher concentrations during summer, and show positive correlations between total dicarboxylic acid concentrations and oxidant concentrations ( $NO_x$ ,  $SO_2$ ,  $O_3$ ). The similar seasonal trend of dicarboxylic acids in Wuhan is mostly caused by an enhanced emission of secondary photochemical products in warm season (Huang *et al.*, 2005).

Oxalic acid (di- $C_2$ ) was the dominant dicarboxylic acid

followed by succinic acid at all three sampling sites. Oxalic acid, ranging from 29.6 to 954.4  $ng/m^3$ , accounted for 27%–48% of nine measured diacids at three sampling sites. Oxalic acid in aerosols is an end product of many precursors including low molecular weight diacids, thus relative abundance of di- $C_2$ /total diacids is indicative of aerosol aging (Wang *et al.*, 2012). Because of the similar molecular structure to succinic acid, malic acid was thought to be produced by the hydroxylation reaction of succinic acid in the atmosphere and finally generate to oxalic acid (Kawamura and Ikushima, 1993). Specifically, at DT and BG site, oxalic acid having the highest relative abundant of all quantified diacids in summer may be due to the more aging aerosols which converted intermediate diacids to oxalic acid. As shown in Table 2, the concentrations of dicarboxylic acids (DCAs) in Wuhan were higher than Beijing and lower than Guangzhou and Nanjing.

The concentration ratios of these diacids, in particular the di- $C_3$ /di- $C_4$  and di- $C_6$ /di- $C_9$  mass ratio, are useful to understand photochemical production of dicarboxylic acids and the source strength of anthropogenic versus biogenic precursors in the atmosphere, respectively. The di- $C_3$ /di- $C_4$  ratio has been reported to be 0.25–0.44 from vehicular emissions (Kawamura and Kaplan, 1987). It has been suggested that succinic acid (di- $C_4$ ) is a precursor of oxalic (di- $C_2$ ) and malonic (di- $C_3$ ) acids (Kawamura *et al.*, 1996a). Therefore, in particles of secondary origin, di- $C_3$ /di- $C_4$  ratio is often found to be notably higher than that range. The ratios of di- $C_3$ /di- $C_4$  in  $PM_{2.5}$  at DT site, approaching to 0.25–0.44, showed that primary emissions especially vehicular emission was an important source at DT site. Specifically,

**Table 4.** Seasonal average concentration of dicarboxylic acid in PM<sub>2.5</sub> at three sampling sites in Wuhan (ng/m<sup>3</sup>).

	SPRING			SUMMER			FALL			WINTER		
	ID	DT	BG	ID	DT	BG	ID	DT	BG	ID	DT	BG
di-C <sub>2</sub>	512.15	246.26	283.92	607.54	571.46	488.55	310.24	222.95	120.08	77.83	39.61	48.20
di-C <sub>3</sub>	216.74	81.61	33.97	167.00	117.48	110.67	94.78	89.09	56.13	15.63	10.14	17.16
di-C <sub>4</sub>	260.32	223.21	231.46	496.14	466.53	276.18	249.93	105.15	78.50	73.93	36.94	47.69
di-C <sub>5</sub>	40.26	46.51	12.45	20.80	18.44	12.48	23.38	32.51	16.41	8.49	3.45	1.87
di-C <sub>6</sub>	96.81	118.58	40.48	30.94	22.34	10.23	33.62	12.69	21.50	10.71	16.90	4.26
di-C <sub>7</sub>	47.13	39.17	79.74	69.61	51.89	30.75	2.61	4.33	1.16	12.71	7.10	3.15
di-C <sub>8</sub>	12.16	15.26	17.99	42.11	52.60	30.82	3.97	4.12	2.26	4.81	3.85	1.91
di-C <sub>9</sub>	98.78	80.97	80.39	73.44	153.74	53.23	18.63	11.87	6.25	4.93	9.76	1.03
di-C <sub>10</sub>	34.94	21.87	31.55	38.82	22.57	23.83	3.82	4.14	2.18	1.96	1.85	1.52
Total	1319.29	873.44	811.95	1546.40	1477.05	1036.74	740.98	486.85	304.47	211.00	129.60	126.79

the lowest value of di-C<sub>3</sub>/di-C<sub>4</sub> (0.2) at DT site in summer confirmed a significant traffic emissions origin in daytime to these dicarboxylic acids (Hsieh *et al.*, 2007; Hsieh *et al.*, 2008; Tsai *et al.*, 2008). The higher ratio of di-C<sub>3</sub>/di-C<sub>4</sub> at DT and BG sites in fall is probably related to enhanced secondary photochemical oxidation production (Kawamura and Ikushima, 1993; Yao *et al.*, 2004). It is worthy to note that the ratio of di-C<sub>3</sub>/di-C<sub>4</sub> at DT and BG sites in summer are not the highest, which may be related to photochemical aging of aerosols in which the malonic acid was further degraded to oxalic acid (Kawamura and Sakaguchi, 1999; Wang *et al.*, 2006; Wang *et al.*, 2012). ID site, located near a coal generating plant, has the highest ratio  $1.177 \pm 0.240$  in summer. It is likely derived from large emissions of VOCs (such as benzene and toluene) precursors which were easily oxidized in high temperature and strong solar radiation condition (Huang *et al.*, 2005; Barsanti *et al.*, 2006). Lower ratios (0.25–0.44, average 0.35) were observed in vehicular exhaust than those in the ambient air because malonic acid is thermally less stable than succinic acid in terms of structure in internal combustion (Kawamura and Kaplan, 1987). As show in Fig. 4, the di-C<sub>3</sub>/di-C<sub>4</sub> ratio in Wuhan is much lower than 3, which is used as an index for secondary formation of dicarboxylic acids (Kawamura and Sakaguchi, 1999; Yao *et al.*, 2004). These results suggest that primary exhaust emission was an important source of dicarboxylic acids as well as secondary formation. The di-C<sub>3</sub>/di-C<sub>4</sub> ratio in this study is much lower than those from remote marine aerosols, where malonic acid is photochemically produced during long-range transport from continents to the marine atmosphere, and malonic acid has less net loss than succinic acid (Kawamura and Sakaguchi, 1999; Fu *et al.*, 2013).

The azelaic acid has been proposed as an unique tracer of photochemical oxidation of biogenic unsaturated monocarboxylic acids which generally contain a double bond at the C<sub>9</sub> position (Kawamura and Gagosian, 1987) and adipic acid has been proposed as one of the products by oxidation of anthropogenic cyclohexene (Kawamura and Gagosian, 1987; Kawamura and Ikushima, 1993). The ratio of di-C<sub>6</sub>/di-C<sub>9</sub> is often used as a potential indicator of source strength of anthropogenic and biogenic precursors to the aerosol diacids. Interestingly, the lowest value of di-C<sub>6</sub>/di-C<sub>9</sub> was recorded in summer followed by spring (Fig. 5), suggesting that the relative contribution of anthropogenic to

biogenic inputs in summer is much less significant. These may be due to the strong microbial activities in summer. It also can be confirmed by the highest ratio of >C<sub>22</sub> homologues to <C<sub>20</sub> homologues in monocarboxylic acids.

#### Source Apportionment Using PMF

Positive matrix factorization (PMF) is a factor analysis method that utilizes non-negativity constraints for the analysis of environmental data and associated error estimates. PMF solves the mass balance equations for each observation  $x_{ij}$  made for the  $j$ th species on the  $i$ th day. The model assumes factor profiles  $f_{kj}$  consisting of the  $j$ th species in the  $k$ th factor, and factor contributions  $g_{ik}$  consisting of the  $k$ th factor on the  $i$ th day. Mathematically stated, the mass balance equations are as follows:

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (2)$$

where  $e_{ij}$  is the residual concentration for each observation. By incorporating an uncertainty for each observation  $s_{ij}$ , a function of the residual and uncertainty is created and is minimized using weighted least-squares.

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left( \frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{s_{ij}} \right)^2 \quad (3)$$

The PMF model seeks to minimize this function. The theoretical minimum Q value is on the order of the number of observations. The model requires data for all concentration and uncertainty values for all  $j$  species and  $i$  days. Data confidence can be maintained by adjusting the uncertainties for questionable observations. This allows the user to downgrade the importance of these data in the least-squares fit. For this study, the U.S. EPA PMF 3.0 was used, which is based on the multilinear engine ME-2 developed by Paatero (Paatero *et al.*, 1999).

In this study, we use 29 variables include C<sub>11</sub>–C<sub>30</sub> monocarboxylic acids, oleic acid and di-C<sub>2</sub>, di-C<sub>3</sub>, di-C<sub>4</sub>, di-C<sub>6</sub>, di-C<sub>9</sub> diacids, and three organic tracer (levoglucosan, cholesterol, phthalic acid). The levoglucosan, ranging from 1.2 to 1394.6 ng/m<sup>3</sup> (average 178.3 ng/m<sup>3</sup>), has a high

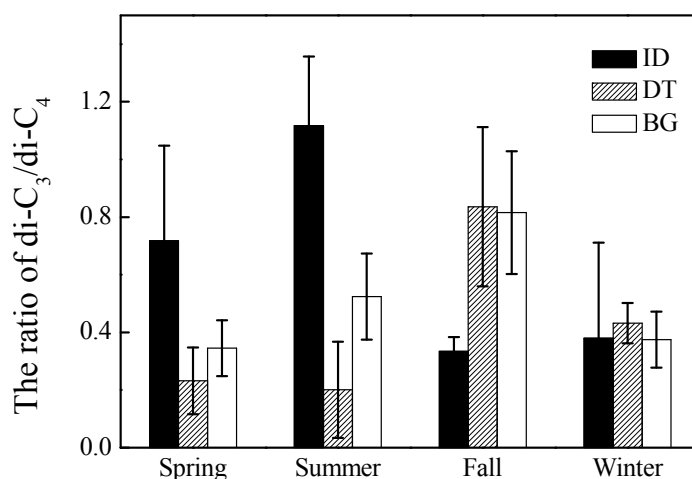


Fig. 4. Seasonal average ratio of di-C<sub>3</sub>/di-C<sub>4</sub> at each site in four seasons.

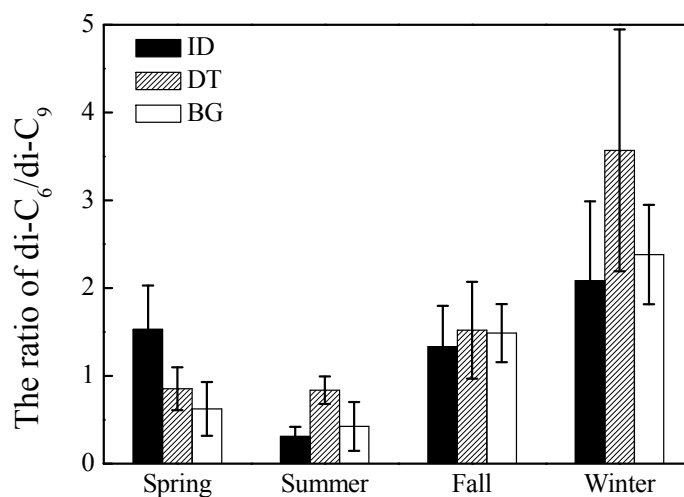


Fig. 5. Seasonal average ratio of di-C<sub>6</sub>/di-C<sub>9</sub> at each site in four seasons.

concentration in fall and winter and lower concentration in summer. The concentration of cholesterol was from 0.4 to 101.6 ng/m<sup>3</sup> (average 15.3 ng/m<sup>3</sup>) and had no obvious seasonal variation. The phthalic acid, ranging from 10.2 to 50.2 ng/m<sup>3</sup> (average 15.3 ng/m<sup>3</sup>), also did not show clear seasonal trend. Allocating uncertainty appropriately to the observed data is an important part of the analysis because the application of the PMF model depends mainly on estimated uncertainties. In this study, measurement uncertainties were used for the error estimates of the measured values; missing data were replaced by the geometric mean of corresponding species and four times of geometric mean was taken as the corresponding error estimates. Data below the minimum detection limit (MDL) were replaced by half the MDL and the corresponding uncertainty was set to 5/6 times the MDL (Polissar *et al.*, 1998). The theoretical Q is not calculated by EPA PMF but can be approximated by the user as  $nm - p(n + m)$ , where  $n$  is the number of species,  $m$  is the number of samples in the data set, and  $p$  is the number of factors fitted by the model (Norris *et al.*, 2008). The critical point in a PMF 3.0 run is to minimize the object function,

Q (Robust). Since the number of measurement days at all three sampling sites were 56 with 29 species, Q (Robust) was calculated as  $1624 - 85p$ . After several attempts, we finally obtain 4 factors at ID site, 3 factors at DT and BG site. So the theoretical Q values were 1284, 1369 and 1369 in ID, DT and BG, respectively. The minimized values of Q (Robust) were 1335, 1463 and 1501 for at the ID, DT and BG site, respectively. These values showed that Q (Robust)s were minimized adequately, because the convergence of the appropriate run was considered as satisfactory by PMF 3.0. Thus, appropriate numbers of factors were obtained. The robust mode was also used to reduce the effects of extreme values in the analysis, and the FPEAK parameter (Paatero *et al.*, 2002) was applied to control rotational ambiguity. In this study, FPEAK value is 0.3 which show a small increase in Q value. The details of the PMF results included intercepts, slopes,  $r^2$  values and signal to noise ratios (S/N). All of the species' values met the performance requirements of the PMF, which are close to 0 for intercept, close to 1 for slope and  $> 0.6$  for  $r^2$ . Additionally, S/N and residuals were appropriate for reliable PMF run.

### Industry Site (ID)

The source profiles of the factors at industry site are given in Fig. 6. The columns show the mass contribution of the species to the factor in  $\text{ng}/\text{m}^3$ , and the diamonds represent the percentage of species in the factor. The first factor has been associated to “meat cooking” activities, showing strong connections with oleic and cholesterol which are the typical tracers of meat cooking activities (Rogge *et al.*, 1991; Schauer *et al.*, 1999a). The second factor was identified as “plant waxes” since it contained the  $\text{C}_{20}$ – $\text{C}_{30}$  monocarboxylic acids which are from vascular plant wax (Simoneit and Mazurek., 1982; Rogge *et al.*, 1993c). The third factor is mainly dominated by  $\text{C}_{11}$ – $\text{C}_{20}$  monocarboxylic acids. These monocarboxylic acids have been considered as good markers of “coal combustion” (Rogge *et al.*, 1993b). The last factor was selected as the “secondary products” characterized by high concentrations and contributions of dicarboxylic acids which were mainly formed through photochemical reactions in the atmosphere (Kawamura *et al.*, 1996b).

As shown in Fig. 9, the performance of PMF in predicting

organic acids concentrations is quite well and explains 94.26% of the measured organic acids concentration. The coal combustion ( $0.44 \mu\text{g}/\text{m}^3$ , 35.90%) made major contribution to all quantitative organic acids followed by plant waxes ( $0.35 \mu\text{g}/\text{m}^3$ , 28.80%) at ID site. Secondary products ( $0.26 \mu\text{g}/\text{m}^3$ , 21.30%) and meat cooking ( $0.17 \mu\text{g}/\text{m}^3$ , 14.0%) account for relative small contribution to organic acids at ID site.

### Downtown Site (DT)

Similar to industry site, three factors were determined: vehicle emissions ( $0.38 \mu\text{g}/\text{m}^3$ , 46.70%), plant waxes ( $0.25 \mu\text{g}/\text{m}^3$ , 31.00%) and secondary products ( $0.18 \mu\text{g}/\text{m}^3$ , 22.30%) at downtown site. The minimized value of  $Q$  (Robust 1463) was close to  $Q$  (True 1369). The total calculated organic acids accounted for 90.74% of the measured organic acids concentration. Factor 1, with high concentration and contribution of  $\text{C}_{11}$ – $\text{C}_{18}$  monocarboxylic acids and phthalic acid, revealed that emissions came from vehicles (Kawamura and Kaplan, 1987). Similar to industry site, plant waxes and secondary products were the other two factors (Fig. 7).

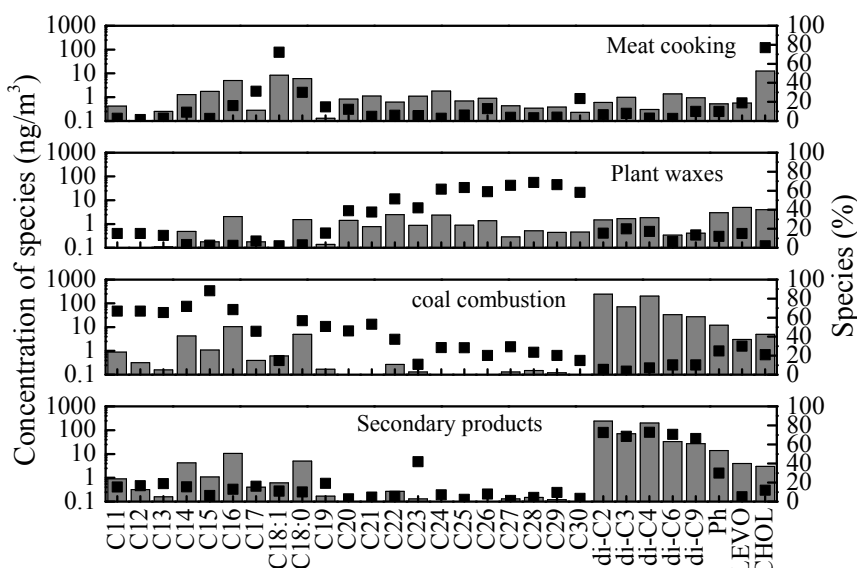


Fig. 6. Source profiles of concentration and percentage of species derived from PMF at ID site.

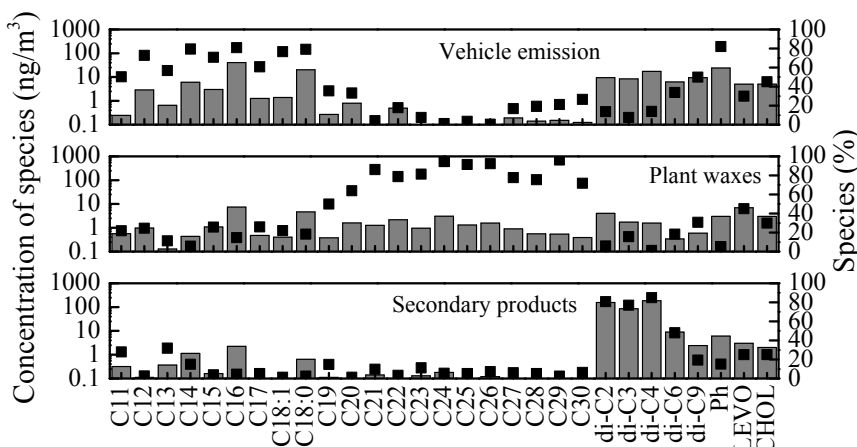


Fig. 7. Source profiles of concentration and percentage of species derived from PMF at DT site.



*Botanical Garden (BG)*

There were three factors at BG site, which is located in the downwind of industry site. Similar to industry site and downtown site, plant waxes (0.21  $\mu\text{g}/\text{m}^3$ , 32.00%) and secondary products (0.16  $\mu\text{g}/\text{m}^3$ , 24.80%) were also two factors. Although source tests of biomass combustion show greater emissions of palmitic acid than tetracosanoic acid, these source tests are typically done in fireplaces or enclosed fireboxes to enable quantification of total particulate emission rates (Rogge *et al.*, 1998; Schauer *et al.*, 1998). Tetracosanoic acid can be the most abundant monocarboxylic acids in campfires or forest fires (Simoneit *et al.*, 2000).

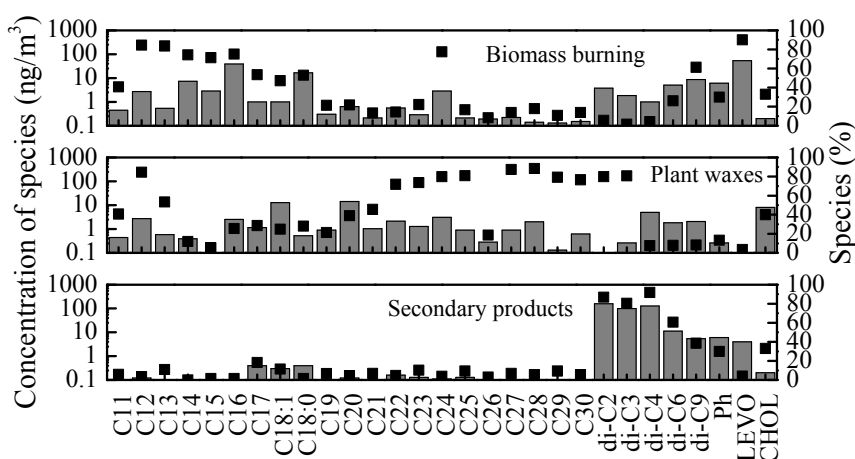
Except with high concentration and contribution of  $\text{C}_{12}$ – $\text{C}_{18}$  monocarboxylic acids and tetracosanoic acid, levoglucosan which has been shown to be an excellent molecular marker for tracking emissions from biomass burning (Simoneit and Elias, 2001) show a high concentration in factor 1 too. These revealed that emissions from biomass burning such as grass, cereal straw and garden residues (Rogge *et al.*, 1998; Hays *et al.*, 2002; Oros *et al.*, 2006; Zhang *et al.*, 2007; Gonçalves *et al.*, 2011). This factor contributes 43.20% (0.28  $\mu\text{g}/\text{m}^3$ ) of all quantitative organic acids in botanical garden site (Fig. 8). Three factors contribute 91.59% of the measured

organic acids concentration for the PMF solution.

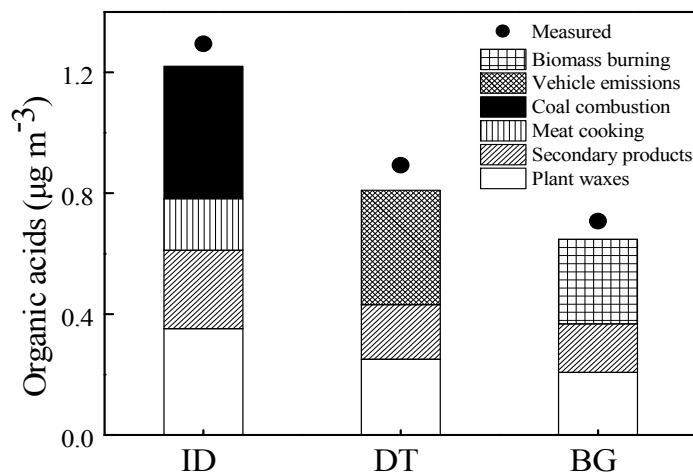
**CONCLUSIONS**

A homologous series of monocarboxylic acids ( $\text{C}_{11}$ – $\text{C}_{32}$ ) and dicarboxylic acids ( $\text{C}_2$ – $\text{C}_{10}$ ) were determined in atmospheric  $\text{PM}_{2.5}$  samples collected at industry, downtown and botanical garden sites in Wuhan. One year study showed that palmitic acid and stearic acid were the most abundant monocarboxylic acids, accounting for 32.4%–62.4% (average 51.8%) of all quantified monocarboxylic acids. Oxalic acid was the most abundant dicarboxylic acid, followed by succinic and malonic acids. The low value of di- $\text{C}_3$ /di- $\text{C}_4$  in Wuhan implies that primary exhaust such as vehicle emissions and meat cooking were the dominant sources of dicarboxylic acids. The lowest values of di- $\text{C}_6$ /di- $\text{C}_9$  in summer suggest that biogenic source input in summer was much more significant.

Furthermore, PMF analysis revealed that the coal combustion, traffic-related emissions, plant waxes and biomass burning were the major primary sources of carboxylic acids in  $\text{PM}_{2.5}$ . Meanwhile, the secondary photochemical products contribute approximately 20% of organic acids in Wuhan.



**Fig. 8.** Source profiles of concentration and percentage of species derived from PMF at BG site.



**Fig. 9.** Distribution of organic acids among the factors for the PMF solution at three sampling sites.

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