

Molecular distributions of diacids, oxoacids and α -dicarbonyls in summer- and winter-time fine aerosols from Tianjin, North China: Emissions from combustion sources and aqueous phase secondary formation

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Abstract

To understand the characteristics and sources of water-soluble organic aerosols (OA) in North China, we studied diacids, oxoacids and α -dicarbonyls in summer- and winter-time fine (PM) aerosols collected from Tianjin. Oxalic (C) acid found to be the most abundant diacid species, followed by succinic (C), malonic (C) and sebacic (C) acids, respectively. Glyoxylic (ω C) was the most abundant oxoacids followed by pyruvic acid. Concentrations of total diacids, oxoacids and α -dicarbonyls in winter were 2-3 times higher than those in summer, but their mass fractions in PM were exactly the opposite. On average, total diacids carbon accounted for 2.93% in total carbon and 3.31% in organic carbon (OC) in summer and 1.79% and 1.98%, respectively, in winter. Their contribution to water-soluble OC was almost same in both seasons (5.46% and 5.31%, respectively). Molecular distributions, mass ratios of selected diacid (C, C, M, F C, Ph and C) species and the linear relations among the selected species (including Σ C-C and Σ C-C) and with inorganic markers (K and SO) implied that the diacids and related compounds are mainly originated from coal combustion and biomass burning emissions and produced in the atmosphere by both photochemical reactions at regional scale in both the seasons and aging during long-range transport, particularly in summer. This study also revealed that diacids and related compounds and WSOC are increased with increasing SO and they produced in aqueous phase, warranting the need of further reduction in SO and NO to control the water-soluble OA loading over North China.

1 **Molecular distributions of diacids, oxoacids and α -dicarbonyls in summer-**
2 **and winter-time fine aerosols from Tianjin, North China: Emissions from**
3 **combustion sources and aqueous phase secondary formation**

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8 **Key Points:**

- 9 • We characterized diacids and related compounds in summer- and winter-time fine
10 aerosols (PM_{2.5}) from Tianjin, North China.
11 • Coal combustion and biomass burning emissions and subsequent secondary processes
12 are the major sources of organic aerosols in North China.
13 • Aqueous phase secondary processes are the major formation pathways of water-soluble
14 organic aerosols and their loading enhanced in winter.

15 Abstract

16 To understand the characteristics and sources of water-soluble organic aerosols (OA) in
17 North China, we studied diacids, oxoacids and α -dicarbonyls in summer- and winter-time
18 fine (PM_{2.5}) aerosols collected from Tianjin. Oxalic (C₂) acid found to be the most abundant
19 diacid species, followed by succinic (C₄), malonic (C₃) and sebacic (C₈) acids, respectively.
20 Glyoxylic (ω C₂) was the most abundant oxoacids followed by pyruvic acid. Concentrations
21 of total diacids, oxoacids and α -dicarbonyls in winter were 2~3 times higher than those in
22 summer, but their mass fractions in PM_{2.5} were exactly the opposite. On average, total diacids
23 carbon accounted for 2.93% in total carbon and 3.31% in organic carbon (OC) in summer and
24 1.79% and 1.98%, respectively, in winter. Their contribution to water-soluble OC was almost
25 same in both seasons (5.46% and 5.31%, respectively). Molecular distributions, mass ratios
26 of selected diacid (C₃, C₄, M, F C₆, Ph and C₉) species and the linear relations among the
27 selected species (including \sum C₂-C₄ and \sum C₈-C₁₂) and with inorganic markers (K⁺ and SO₄²⁻)
28 implied that the diacids and related compounds are mainly originated from coal combustion
29 and biomass burning emissions and produced in the atmosphere by both *in-situ*
30 photochemical reactions at regional scale in both the seasons and aging during long-range
31 transport, particularly in summer. This study also revealed that diacids and related
32 compounds and WSOC are increased with increasing SO₄²⁻ and they produced in aqueous
33 phase, warranting the need of further reduction in SO₂ and NO_x to control the water-soluble
34 OA loading over North China.

35 Keywords

36 Diacids and related compounds, Coal and biomass combustion, Aqueous phase secondary
37 formation, Fine aerosols, North China

38 1 Introduction

39 Water-soluble organic aerosols (OA) that make up a substantial fraction of total OA mass;
40 up to 40%, have serious impacts on the Earth's climate system, preferably by indirect radiative
41 forcing (Novakov & Penner, 1993; Ramanathan et al., 2001), and cause adverse effects on
42 human health (Baltensperger et al., 2008), and also play an important role in atmospheric
43 chemistry (Andreae & Crutzen, 1997; Kolb & Worsnop, 2012). Homologues series of
44 dicarboxylic acids, oxoacids and α -dicarbonyls account for a dominant fraction of water-
45 soluble organics (Kawamura & Bikkina, 2016). High abundance of diacids can increase the
46 acidity of aerosols, which could promote the cloud condensation nuclei (CCN) formation and
47 reduce the visibility (Facchini et al., 1999). Because diacids and related compounds are highly
48 water-soluble, their presence on particle surface alters the hygroscopic behavior of the particles
49 (Saxena et al., 1995) and thus, their capacity to act as CCN (Prenni et al., 2001) and regulate
50 microstructure of the clouds (Asa-Awuku et al., 2011). Enhanced CCN number concentrations
51 in the atmosphere should result in the increase of indirect radiative forcing by aerosol, causing
52 a more reflective clouds (Twomey, 1977) and less precipitation (Albrecht, 1989).

53 In addition, diacids and related compounds, which possess low vapor pressure are involved
54 in fog formation and acid precipitation. They participate in various physical and chemical
55 reactions in the atmosphere. *For example*, Folkers et al. (2003) reported that unlike uncoated
56 NH_4HSO_4 particles, the NH_4HSO_4 particles coated with an organic substance containing a
57 diacid have a reduced reaction absorption coefficient for N_2O_5 (one of the main intermediates
58 for NO_x removal in the atmosphere), which increases oxidative capacity of the particles. This
59 indicates that the organic surface inhibits the transfer of N_2O_5 into NH_4HSO_4 core.
60 Consequently, diacids and related compounds play an important role in the climate change.
61 However, studies on the composition and molecular distributions of diacids and related
62 compounds and identification of their secondary formation and transformation pathways are
63 scarce. Therefore, the study of low molecular weight (LMW) diacids and related compounds
64 has become an issue of growing interest in recent times.

65 Diacids and related compounds with high abundance of oxalic (C_2) acid have been
66 recognized as ubiquitous constituents in atmospheric aerosols in various environments such as
67 urban, rural, mountain, polar and marine (Kawamura & Bikkina, 2016). The abundance of total
68 diacids-carbon to total organic carbon (OC) is reported to be 1-3% in urban areas (Kawamura
69 & Ikushima, 1993; Kawamura & Yasui, 2005; Miyazaki et al., 2009; Pavuluri et al., 2010) and
70 up to 16% and 24 % in the remote and tropical marine atmosphere, respectively (Fu et al., 2013;
71 Kawamura & Sakaguchi, 1999). Diacids and related compounds can be emitted directly into
72 the atmosphere from primary sources such as fossil fuel combustion, biomass burning and meat
73 cooking, and formed in the atmosphere by photochemical oxidation of their precursors of both
74 anthropogenic and biogenic origin in gas and liquid phases (Kawamura & Bikkina, 2016;
75 Kawamura et al., 1996). Their relative contributions from primary and secondary sources
76 depend on the types of emissions, meteorology and oxidation capacity of the atmosphere at
77 local scale. In addition, diacids and related compounds are subjected for further photochemical
78 processing (aging) during long-range transport in the atmosphere, resulting multiple
79 generations of more oxygenated species; e.g., carbonyls to carboxylic acids and diacids and
80 long-chain diacids to their lower homologues (Kawamura & Ikushima, 1993; Tilgner &
81 Herrmann, 2010).

82 To understand characteristics, origins and photochemical formation and transformations
83 of OA during long-range atmospheric transport, many observational studies have been carried
84 out over the past two decades, but they are limited to certain regions and not sufficient enough
85 at regional to global scale. In East Asia, high aerosol loadings are common and often suffers
86 from haze events due to enhancing development of urbanization and industrialization in recent
87 times, particularly over China (Carmichael et al., 2009; Huang et al., 2014; Zhang et al., 2012).
88 Despite a great attention has been paid on Chinese aerosol studies through ground-based
89 measurements at different locations and large-scale field experiments, the studies on molecular
90 characterization of OA are very limited (Cao et al., 2007; Fu et al., 2008; Fuzzi et al., 2006;
91 Huang et al., 2014; Nakajima et al., 2007; Wang et al., 2007), and in particular, the studies on
92 more oxygenated species such as diacids and related compounds are sparse (Ho et al., 2007;
93 Wang et al., 2002; Zhang et al., 2016; Zhao et al., 2018). Hence, it is highly necessary to study
94 the characteristics of diacids and related compounds in atmospheric aerosols at different

95 locations, particularly over North China, where the aerosol loading is much high compared to
96 that in other parts of China.

97 In this study, we report the molecular distributions of diacids, oxoacids and α -dicarbonyls
98 in fine (PM_{2.5}) summer- and winter-time aerosols collected from Tianjin, North China, which
99 can be considered as an ideal location to collect the air masses originated from the oceanic
100 region in summer and Siberia passing over Mongolia and northern parts of mainland China in
101 winter. We discuss the sources of diacids and related compounds over the North China region
102 including their *in-situ* secondary formation at local scale and photochemical processing (aging)
103 during long-range atmospheric transport, based on mass ratios of selected species and their
104 linear relations with marker ions together with the air mass trajectories.

105 **2 Experimental**

106 2.1 Site Description

107 Tianjin is a typical metropolis and largest coastal city in North China, located at 39°N and
108 117°E on the lower reaches of Haihe River and adjacent to the Bohai Sea, with a population of
109 approximately 15 million (<https://en.wikipedia.org/wiki/Tianjin>). The weather is influenced by
110 the East Asian monsoon prevailing with cold and dry air in winter and hot and humid air in
111 summer. Although the consumption of coal for domestic energy has been banned in some cities
112 in North China, its consumption for industrial terminal energy accounts for about 66% to the
113 total energy consumption, which is higher than that in Beijing and Shanghai (Meng et al., 2015).
114 The agricultural activity is significant in northern parts of Tianjin region, and it is also covered
115 with mountains and dense forests. Tianjin is one of the most rapidly developing regions in
116 China and has become an economic center in northern China with an annual growth of GDP at
117 14.5% (Bian et al., 2007). Furthermore, the East Asian monsoon, which forms as a result of
118 the thermal difference between the Asian continent and the Pacific Ocean, controls the source
119 regions and composition of the air masses transported over to Northeast China. Therefore,
120 Tianjin is considered as an ideal location for collecting the air masses delivered from Siberia,
121 parts of China, and surrounding oceans as well as local emissions.

122 2.2 Aerosol Sampling

123 Fine aerosol (PM_{2.5}) sampling was performed at Tianjin University, Nankai district located
124 in central Tianjin. The sampling point is ~ 600 meters away from the road and no industries
125 are located in the immediate vicinity. PM_{2.5} samples were collected on the rooftop of a six-
126 story building (~20 m above ground level (AGL) using precombusted (at 450°C for 6 hours)
127 quartz fiber filters (Pallflex 2500QAT-UP) and a high-volume sampler (TISCH Environmental
128 TE-6070DX) with a flow rate of 68 m³ h⁻¹ on day- and night-time basis in summer (6-19 July,
129 $n = 27$) and winter (9 November-22 December, $n = 85$) 2016. Before sampling in each season,
130 sampler was calibrated and run for one-day as test period and then actual sampling was started.
131 One blank sample was also collected in each season, placing the filter on filter hood for minutes
132 without turning on the pump. The filter samples were wrapped in aluminum foil and sealed in
133 zip-lock plastic bags and then stored in freezer at -20°C until analysis.

134 2.3 Measurements of Diacids and Related Compounds

135 Diacids, oxoacids and α -dicarbonyls in PM_{2.5} were determined following the method
136 reported elsewhere (Kawamura & Ikushima, 1993; Pavuluri et al., 2010). In brief, an aliquot
137 of filter sample (20 mm disc in diameter in winter, 30 mm disc in summer), extracted into
138 Milli-Q water (10 ml) for 3 times under ultrasonication for 10 min each. The extracts were
139 filtered through pasteur pipette loaded with small amount of quartz wool to remove the filter
140 debris and adjusted their pH to 8.4~9.5 using 0.1 M KOH and then concentrated to nearly
141 dryness under rotary evaporation. The diacids and related compounds were derivatized to their
142 corresponding dibutyl esters and/or acetals, by reacting with 14% BF₃/n-butanol at 100°C for
143 one hour. The derivatized species were dissolved in *n*-hexane and washed with Milli Q water
144 and 0.2 ml acetonitrile to remove the unreacted BF₃ and other contents and then concentrated
145 to dryness under rotary evaporation followed by N₂ blow. The derivatized dibutyl esters and/or
146 acetals were finally dissolved into *n*-hexane (100 μ l) and then injected into split/splitless
147 GC/FID (Agilent 7980) equipped with an HP-5 capillary column (0.2 mm \times 25 m, 0.5 μ m film
148 thickness). Identification of various compounds were confirmed by GC/mass spectrometer,
149 whose sampling port temperature and increasing temperature program is same to that of GC-
150 FID. Recoveries of authentic standards of oxalic (C₂), malonic (C₃), succinic (C₄) and adipic
151 (C₆) acids spiked to a pre-combusted quartz fiber filter were 98%, 71%, 85% and 89%,
152 respectively. The analytical errors in duplicate analysis of filter samples was within 5%. The
153 field blank filters were also analyzed following the same procedure and found small peaks for
154 oxalic (C₂), succinic (C₄) and pyruvic (Pyr) acids and glyoxal (Gly), but their concentrations
155 were less than 5% of the actual samples. Final concentrations of the species measured in this
156 study were corrected for the field blanks.

157 2.4 Inorganic Ions

158 Inorganic ions were measured using the extract of an aliquot of filter sample extracted
159 into Milli Q water under ultrasonication for 30 minutes and filtered through syringe filter
160 (0.22 μ m) and ion chromatograph (ICS 5000+). A mixture of 1.8 mM Na₂CO₃ and 17 mM
161 NaHCO₃ and 40 mM H₂SO₄ were used as eluent at a flow rate of 1.2 mL min⁻¹ and suppressor,
162 respectively, for anion measurement, respectively. 4 mM H₃PO₄ was used as eluent at a flow
163 rate of 1.0 mL min⁻¹ for cation measurement (Pavuluri et al., 2011). A calibration curve was
164 evaluated for each sequence by the analyses of a set of authentic standards and the analytical
165 errors in duplicate analysis were within 6%. The nss-SO₄²⁻ and nss-K⁺ were calculated using
166 Na⁺ as a reference for sea-salt.

167 2.5 Meteorology

168 Weather data such as temperature, humidity, wind and rainfall were monitored using
169 weather station installed beside the sampler during the sampling period and the data were
170 averaged for 12-hours corresponding to each sample period. During the summer campaign, the
171 average temperature was 21.1°C in daytime and 26.3°C in nighttime and the relative humidity
172 (RH) was 45.9% and 70.5%, respectively. They were 6.88°C and 54.7% in daytime and 5.11°C
173 and 61.7% in nighttime, respectively, during the winter campaign. The average wind was

174 mainly flown from southeast region and the weather was mostly sunny and precipitation was
175 not frequent in summer, whereas the fog formation was significant, visibility was poor, and
176 snowfall often occurred in winter.

177 2.6 Backward Air Mass Trajectories

178 Seven-day backward air mass trajectories arriving at 500 m AGL over Tianjin were
179 computed using Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model of
180 the National Oceanic and Atmospheric Administration (NOAA). The representative air mass
181 trajectories were provided elsewhere (Wang et al., 2018). In summer, the air masses were
182 originated from the Pacific Ocean and passed over the Bohai Sea and eastern parts of the
183 Chinese mainland. Whereas in winter, they were originated from Eurasia and passed over
184 Siberia, Mongolia and northern parts of China. However, unlike in summer, the air parcels
185 were travelled at very low altitude for most of the time in winter.

186 3 Results and Discussion

187 3.1 Molecular Composition and Distributions

188 A homologous series of saturated normal diacids (C₂-C₁₂) and branched diacids (*iso*C₄-
189 C₆) were detected in both summer- and winter-time Tianjin aerosols (PM_{2.5}). In addition, we
190 found unsaturated aliphatic (maleic (M), fumaric (F) and methylmaleic (mM)) and aromatic
191 (phthalic (Ph), isophthalic (*i*Ph) and terephthalic (*t*Ph)) acids and diacids with an additional
192 functional (carbonyl) group (ketomalonic (kC₃) and 4-ketopimelic (kC₇) acids) in the PM_{2.5}.
193 C₂-C₉ ω -oxoacids, excluding C₆ oxoacid, and an α -oxoacid (Pyr) and α -dicarbonyls (Gly and
194 methylglyoxal (mGly)) were also detected in these samples. Concentrations of individual
195 diacids, oxoacids and α -dicarbonyls and their relative abundances to the total diacids, oxoacids
196 and α -dicarbonyls, respectively, in Tianjin summer- ($n = 27$) and winter-time ($n = 81$) PM_{2.5}
197 are summarized in Table 1. Molecular distributions of diacids and related compounds in day-
198 and night-time in both the seasons are depicted in Fig. 1.

199 Concentrations of total diacids ranged from 185 ng m⁻³ to 2874 ng m⁻³ with an average of
200 879 ± 586 ng m⁻³ in the Tianjin PM_{2.5} during the whole campaign ($n = 108$). While those of
201 oxoacids and α -dicarbonyls were 23.8-767 ng m⁻³ (ave. 234 ± 179 ng m⁻³) and 4.39-286 ng m⁻³
202 (49.4 ± 51.1 ng m⁻³), respectively. Molecular distributions of the measured diacids and related
203 compounds were characterized by a predominance of C₂ diacid followed by glyoxylic (ω C₂),
204 Ph, C₄ and *t*Ph acids, respectively. Pyr was found to be the sixth most abundant species
205 followed by malonic (C₃), oxobutanoic (ω C₄) and azelaic acid (C₉), respectively, during the
206 campaign. Relative abundance of C₂ diacid to total diacids ranged from 10.6% to 58.4% with
207 an average of $38.9 \pm 11.0\%$ followed by Ph (ave. $10.0 \pm 4.49\%$), C₄ ($8.54 \pm 1.94\%$), *t*Ph (7.68
208 $\pm 5.50\%$), C₃ ($5.42 \pm 1.86\%$) and C₉ ($3.99 \pm 1.84\%$) diacids, respectively, during the whole
209 campaign ($n = 108$). While, on average, ω C₂ acid accounted for $33.1 \pm 15.7\%$ to total oxoacids
210 followed by Pyr ($25.7 \pm 12.0\%$), ω C₄ ($17.7 \pm 7.77\%$) and ω C₃ ($8.35 \pm 4.53\%$) acids,
211 respectively. Both Gly and mGly were almost equally abundant with a relative abundance of
212 $45.1 \pm 20.3\%$ and $54.9 \pm 20.3\%$ to total α -dicarbonyls, respectively.

213 **Table 1**

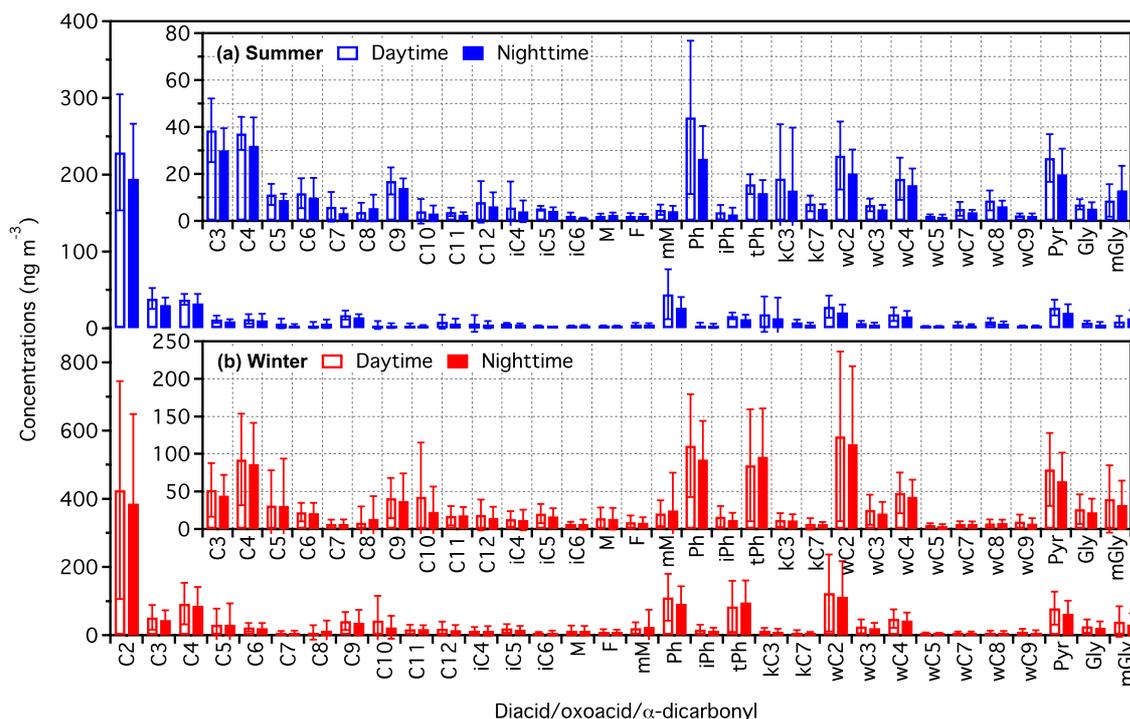
214 *Summary of Concentrations of Diacids, Oxoacids, and α -Dicarbonyls and Their Relative Abundances in*
 215 *Total Diacids, Oxoacids, and α -Dicarbonyls in PM_{2.5} Collected from Tianjin, North China During Winter*
 216 *and Summer, 2016a.*

Compounds	Summer (n = 27)				Winter (n = 85)			
	Concentration (ng m ⁻³)			Relative Abundance (%)	Concentration (ng m ⁻³)			Relative Abundance (%)
	Range	Med	Ave. \pm SD	Ave. \pm SD	Range	Med	Ave. \pm SD	Ave. \pm SD
	<i>Diacids</i>							
Oxalic, C ₂	90.5–371	208	213 \pm 74.6	48.3 \pm 6.85	42.2–1365	386	405 \pm 290	35.8 \pm 10.4
Malonic, C ₃	15.6–64.9	33.5	34.5 \pm 12.3	7.88 \pm 1.44	7.60–157	44.1	48.2 \pm 32.0	4.60 \pm 1.09
Succinic, C ₄	8.31–56.6	35.6	34.8 \pm 9.94	8.27 \pm 2.35	18.0–275	86.2	89.6 \pm 57.6	8.63 \pm 1.79
Glutaric, C ₅	5.12–22.6	10.6	10.3 \pm 3.82	2.37 \pm 0.70	n.d–416	21.5	31.1 \pm 55.4	2.76 \pm 2.87
Adipic, C ₆	3.51–35.7	8.03	10.9 \pm 7.26	2.44 \pm 1.14	n.d–72.8	21.7	21.8 \pm 13.1	2.19 \pm 0.73
Pimelic, C ₇	0.99–26.7	3.94	4.73 \pm 4.83	1.22 \pm 1.50	n.d–24.2	5.68	6.95 \pm 5.78	0.63 \pm 0.35
Sebacic, C ₈	n.d.–17.8	3.23	4.63 \pm 4.75	1.32 \pm 1.72	n.d–154	3.08	11.0 \pm 26.1	1.63 \pm 4.23
Azelaic, C ₉	7.17–30.3	14.7	15.6 \pm 5.12	3.75 \pm 1.33	4.30–193	35.2	39.3 \pm 32.2	4.07 \pm 1.99
Decanedioic, C ₁₀	1.10–18.0	1.93	3.66 \pm 4.37	0.99 \pm 1.37	n.d–363	6.98	32.7 \pm 56.3	3.92 \pm 6.38
Undecanedioic, C ₁₁	1.10–8.36	3.16	3.29 \pm 1.60	0.82 \pm 0.58	n.d–49.8	18.03	18.2 \pm 11.8	2.17 \pm 1.56
Dodecanedioic, C ₁₂	n.d.–30.0	5.97	7.22 \pm 7.48	1.86 \pm 1.96	n.d–72.9	9.75	17.0 \pm 17.8	1.83 \pm 2.20
Methylmalonic, iC ₄	0.94–44.0	2.93	5.02 \pm 8.46	1.18 \pm 1.62	n.d–70.3	8.59	12.7 \pm 12.0	1.52 \pm 1.62
Methylsuccinic, iC ₅	1.91–7.25	5.21	4.89 \pm 1.34	1.15 \pm 0.26	n.d–56.6	16.3	18.6 \pm 11.7	1.89 \pm 0.76
2-Methylglutaric, iC ₆	0.45–5.35	1.24	1.64 \pm 1.19	0.37 \pm 0.23	n.d–44.6	5.20	6.09 \pm 5.40	0.73 \pm 0.76
Maleic, M	n.d.–4.23	2.19	2.32 \pm 1.00	0.57 \pm 0.31	n.d–71.4	10.1	14.0 \pm 14.2	1.28 \pm 0.65
Fumaric, F	0.68–6.29	1.67	1.92 \pm 1.21	0.47 \pm 0.34	n.d–37.4	7.26	8.85 \pm 7.90	0.78 \pm 0.40
Methylmaleic, mM	n.d.–8.58	4.02	4.53 \pm 2.12	1.12 \pm 0.59	3.06–328	14.5	22.9 \pm 37.4	2.22 \pm 2.75
Phthalic, Ph	2.20–128	36.7	35.6 \pm 26.5	7.51 \pm 4.11	8.72–305	94.3	102 \pm 60.8	10.9 \pm 4.31
Isothalic, <i>i</i> -Ph	n.d.–13.3	2.66	3.28 \pm 2.96	0.75 \pm 0.71	n.d–58.6	12.4	14.1 \pm 12.2	1.25 \pm 0.95
Terephthalic, <i>t</i> -Ph	1.81–23.9	13.9	13.9 \pm 5.21	3.20 \pm 1.05	n.d–372	90.0	90.6 \pm 69.4	9.17 \pm 5.57
Ketomalonic, kC ₃	1.13–93.8	3.08	15.6 \pm 24.6	3.07 \pm 4.91	n.d–35.7	9.49	11.9 \pm 8.56	1.15 \pm 0.56
4-Ketopimelic, kC ₇	1.58–15.8	5.94	6.33 \pm 2.95	1.44 \pm 0.46	n.d–49.1	5.12	6.30 \pm 5.83	0.90 \pm 0.96
<i>Total diacids</i>	254–707	416	437 \pm 133		185–2874	1028	1027 \pm 604	
	<i>Oxoacids</i>							
Glyoxylic, ω C ₂	7.32–59.1	20.5	24.2 \pm 13.0	27.5 \pm 6.70	6.07–400	83.3	118 \pm 108	34.9 \pm 17.3
3-Oxopropanoic, ω C ₃	1.76–11.7	5.43	5.91 \pm 2.42	6.95 \pm 1.51	n.d–85.3	18.4	23.3 \pm 17.8	8.82 \pm 5.08
4-Oxobutanoic, ω C ₄	1.09–38.4	16.6	16.7 \pm 8.09	18.5 \pm 5.95	n.d–103	51.8	45.4 \pm 25.2	17.5 \pm 8.31
5-Oxopentanoic, ω C ₅	0.41–4.75	1.65	1.68 \pm 0.98	1.96 \pm 0.79	n.d–13.9	3.97	4.16 \pm 2.68	2.04 \pm 2.61
7-Oxoheptanoic, ω C ₇	0.72–12.2	4.31	4.48 \pm 2.29	5.97 \pm 4.30	n.d–16.9	5.60	6.58 \pm 3.74	3.35 \pm 3.19
8-Oxo-octanoic, ω C ₈	3.27–21.2	6.99	7.50 \pm 3.59	9.34 \pm 3.72	n.d–17.9	7.21	7.85 \pm 4.80	4.37 \pm 5.97
9-Oxononanoic, ω C ₉	0.77–4.37	2.27	2.33 \pm 0.91	3.35 \pm 2.67	n.d–47.5	7.30	8.64 \pm 8.33	3.56 \pm 3.92
Pyruvic, Pyr	3.03–44.2	23.8	23.5 \pm 10.9	26.4 \pm 8.11	0.18–216	74.9	71.3 \pm 43.9	25.5 \pm 13.1
<i>Total oxoacids</i>	23.8–188	86.1	86.3 \pm 34.7		30.2–767	249	284 \pm 181	
	<i>α-Dicarbonyls</i>							
Gly	0.26–11.0	6.64	6.18 \pm 2.58	42.8 \pm 23.9	1.30–75.8	20.8	24.3 \pm 18.8	45.9 \pm 19.0
mGly	0.95–36.5	8.07	10.8 \pm 8.87	57.2 \pm 23.9	1.88–213	24.8	36.0 \pm 39.1	54.1 \pm 19.0
<i>Total α-dicarbonyls</i>	6.05–47.6	14.3	17.0 \pm 9.58		4.39–286	44.2	60.2 \pm 54.7	

217 ^aAve., average; SD, Standard Deviation; n.d., not detectable.

218 It is of worthy to note that the high abundance of C₄ diacid than that of C₃ diacid in Tianjin
 219 aerosols is a unique feature, because such pattern is generally the opposite to that reported in
 220 continental and marine aerosols, particularly in those photochemically aged during long-range
 221 atmospheric transport (Kawamura & Bikkina, 2016), but similar to that reported in Beijing
 222 aerosols, which were significantly influenced by fossil fuel combustion and waste incineration
 223 (Zhao et al., 2018). Unlike most of the previous reports from different locations over the world
 224 (Kawamura & Bikkina, 2016), the concentrations of normal saturated diacids did not follow a
 225 decreasing trend with increasing carbon chain length, with relatively high loadings of C₁₁ and
 226 C₁₂ diacids than their lower homologues, particularly C₇ and C₈ diacids, in both summer and
 227 winter (Table 1). Furthermore, average concentrations of total diacids, oxoacids and α -
 228 dicarbonyls in Tianjin aerosols were found to be much higher than those (ave. 438 \pm 267, 43.0
 229 \pm 48 and 11.0 \pm 18 ng m⁻³, respectively) reported in Pearl River Delta region, one of the heaviest
 230 haze regions in China (Ho et al., 2011) and Jeju Island, Korea (660, 53.0 and 12.4 ng m⁻³,

231 respectively) (Kawamura et al., 2004), as well as in Arctic aerosols ($\sim 100 \text{ ng m}^{-3}$) (Kawamura
 232 et al., 2010) and in Chichijima Island, a remote marine region (range, 6-550 ng m^{-3} ; ave. 130
 233 ng m^{-3}) (Mochida, 2003). However, they were slightly lower than or comparable to those
 234 reported in Xi'an fine ($\text{PM}_{2.5}$) aerosols (1350, 167 and 37.0 ng m^{-3} , in summer and 2053, 421,
 235 and 120 ng m^{-3} in winter), where high aerosol loading including haze events are common
 236 (Wang et al., 2012). Such results and comparisons suggest that the origins of OA in the Tianjin
 237 region might be different from other and/or their *in-situ* secondary formation should be more
 238 significant.



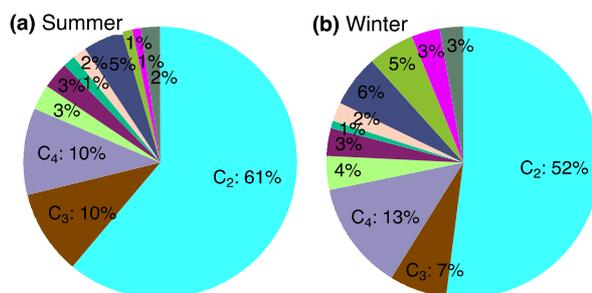
239 **Figure 1.** Molecular distributions of diacids, oxoacids, and α -dicarbonyls in $\text{PM}_{2.5}$ collected on day- and
 240 night-time basis from Tianjin, North China during (a) summer and (b) winter.

241 3.2 Seasonal and Diurnal Variations

242 3.2.1 Saturated Normal and Branched Diacids

243 Concentrations of saturated normal diacids in winter were twice higher, while the
 244 branched diacids were higher by a factor of 3, than those in summer (Table 1). However,
 245 branched C_4 , C_5 and C_6 ($i\text{C}_4$ - $i\text{C}_6$) diacids were less abundant than their corresponding normal
 246 structures in both the seasons (Table 1, Fig. 1). Although C_2 diacid was the most abundant
 247 species in both the seasons, its relative abundance to total normal C_2 - C_{12} diacids was reduced
 248 on average by about 9% from summer to winter (Fig. 2). It is also worth to note that C_4 diacid
 249 was equally abundant to that of C_3 diacid in summer, whereas in winter, it was higher by a
 250 factor of 2 than that of C_3 (Table 1). Their relative abundances to normal diacids were also
 251 showed the same seasonal pattern (Fig. 2). The high abundance of C_4 than that of C_3 diacid is
 252 consistent with that reported for urban aerosols at 14 megacities over China, in which their

253 averages were 79.7 ng m⁻³ and 40.6 ng m⁻³ in winter, where fossil fuel combustion and biomass
 254 burning were considered as major sources of the aerosols (Ho et al., 2007). However, the
 255 relative abundances of C₁₀ and C₁₁ diacids to total normal C₂-C₁₂ diacids were enhanced by 5
 256 and 3 folds, respectively, from summer to winter periods, while that of C₅ and C₉ diacids were
 257 increased by 1% in winter compared to that in summer (Fig. 2). In fact, the concentrations of
 258 C₅ diacid in winter were more than 3 times higher than that in summer.



259 **Figure 2.** Relative abundances of normal saturated diacids in PM_{2.5} from Tianjin, North China in (a) summer
 260 and (b) winter.

261 It is well established that C₄ diacid is produced by photochemical oxidation of unsaturated
 262 fatty acids (Kawamura & Gagosian, 1987) *via* oxoacids as well as by photochemical
 263 transformations of higher homologous diacids (Pavuluri et al., 2015; Tilgner & Herrmann,
 264 2010; Yang et al., 2008). While photochemical oxidation of cyclic olefins significantly
 265 contributes to C₅ and C₆ diacids (Hatakeyama et al., 1987; Kawamura et al., 1996). In fact, the
 266 average concentration of C₆ diacid (Table 1), which has been considered to be a tracer for
 267 anthropogenically derived OA (Kawamura & Ikushima, 1993), in summer is comparable to
 268 that (12.7 ng m⁻³) reported in Hong Kong road side aerosols, whereas in winter, the average C₆
 269 diacid was much higher than that reported in Hong Kong (10.7 ng m⁻³) (Ho et al., 2006) as
 270 well as in Tokyo (ave.14.2 ng m⁻³) (Kawamura & Yasui, 2005), where the input from fossil
 271 fuel combustion is the major source of aerosols. In contrast, C₉ diacid, which can be derived
 272 from unsaturated fatty acids emitted from marine biota and terrestrial plants as well as cooking
 273 emissions and has been considered as a tracer of OA of biogenic origin (Kawamura & Gagosian,
 274 1987), was found to be the fourth most abundant diacids in both summer and winter (Table 1).

275 Such molecular distributions and their seasonal variations suggest that they might have
 276 significantly derived from mixed sources in both the seasons. High relative abundance of C₂
 277 and C₃ diacids in summer than that in winter (Table 1; Fig. 2) indicates that the photochemical
 278 processing of OA during long-range atmospheric transport might be significant in summer
 279 rather than in winter. Furthermore, the concentrations of straight chain diacids were found to
 280 be generally higher in daytime than that in nighttime (Fig. 3a,b), except for C₈ diacid in summer
 281 and C₅, C₇ and C₈ diacids in winter (not shown here). Interestingly, C₂-C₄ diacids showed a
 282 significant diurnal variation in both the seasons (Fig. 3a), indicating that *in-situ* photochemical
 283 oxidation of organics was also more intensive during daytime in the Tianjin atmosphere,
 284 associating with intense solar radiation and high ambient temperature (up to 33.1°C) during
 285 daytime in summer. However, an enhancement in the relative abundance of C₉ and C₁₂ diacids

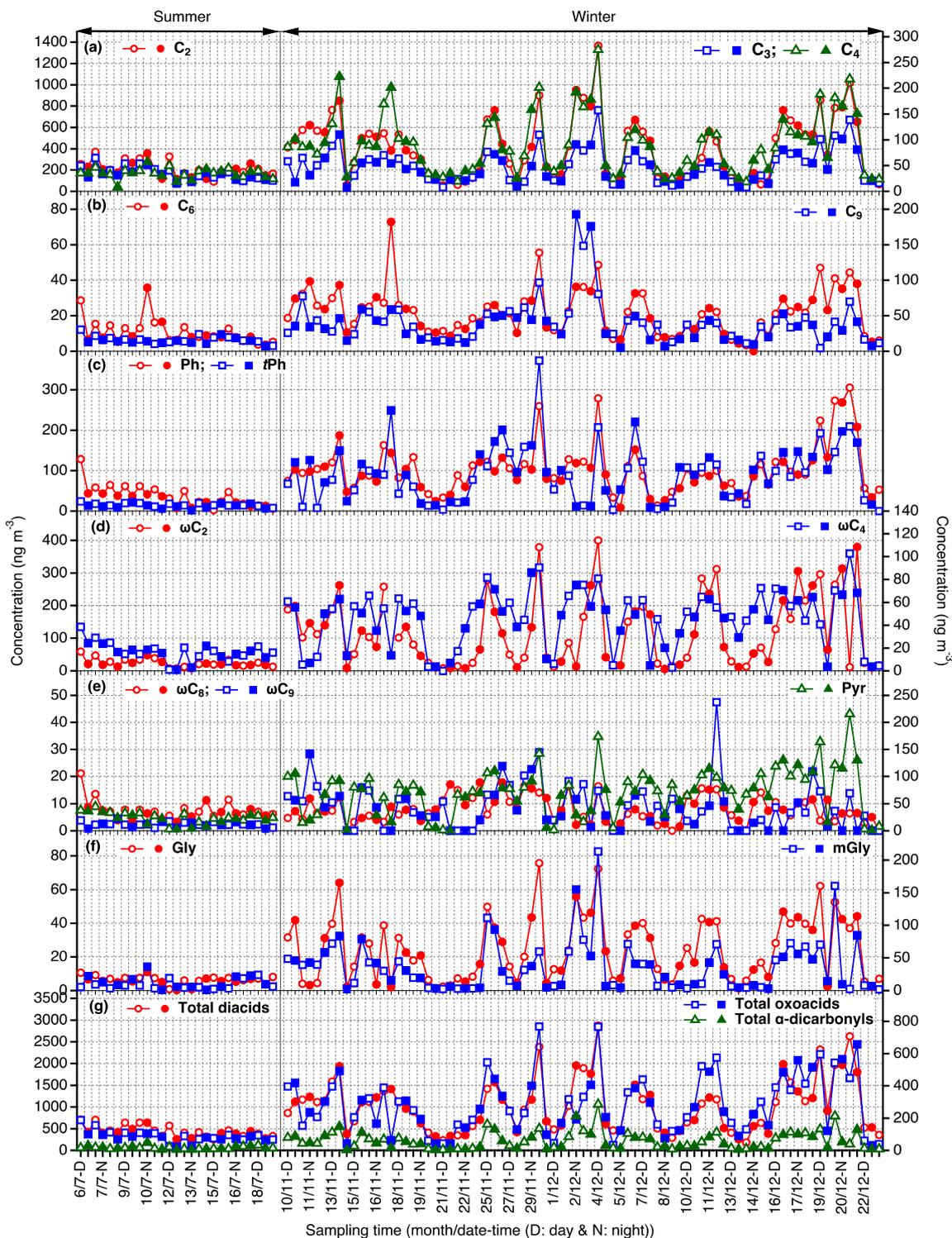
286 and a large increment in that of C₁₀ and C₁₁ diacids from summer to winter, despite the fact
287 that the air masses arrived in Tianjin were originated from the Pacific Ocean during the summer
288 campaign, indicate that the OA should have been significantly derived from the enhanced local
289 emissions, probably biomass burning, rather than biogenic emissions in winter. Alternatively,
290 they might have derived from terrestrial biogenic VOCs and accumulated in the lower
291 atmosphere due to relatively stagnant weather conditions in winter. The branched chain diacids
292 did not show any diurnal changes, suggesting that they should have been derived from other
293 precursors and/or their photochemical formation process are different from the straight chain
294 diacids. In fact, it has been reported that branched chain diacids are considered to be generated
295 *via* photochemical oxidation of methylcycloalkanes (Grosjean & Fung, 1984).

296 3.2.2. *Unsaturated and Multifunctional Diacids*

297 Concentrations of both aliphatic unsaturated (M, F and mM) and aromatic (Ph, *i*Ph and
298 *t*Ph) diacids measured in this study were ~4 times higher in winter than those in summer. Their
299 distributions were characterized by a predominance of Ph followed by *t*Ph and mM acids. Such
300 pattern is similar to that reported in subtropical Okinawa in the Western Pacific Rim (Kunwar
301 & Kawamura, 2014) and Xi'an, China (Cheng et al., 2013). The relative abundances of Ph and
302 *t*Ph acids to total diacids were higher than those in summer (Table 1). Similarly, those of M
303 and F acids were also showed higher abundances in winter compared to that in summer (Table
304 1). The average concentration of Ph acid in winter (Table 1) was slightly higher than that (78.0
305 ng m⁻³) reported in Hong Kong roadside aerosols, where the fossil fuel combustion emissions
306 and their subsequent oxidation has been considered to be the major sources of OA (Ho et al.,
307 2006).

308 Ph acid is mainly derived from photochemical oxidation of aromatic hydrocarbons such
309 as naphthalene that reported to be abundant in some megacities of China. The process of Ph
310 acid formation mainly involves its photochemical production in gas phase and subsequent
311 absorption onto existing particles (Kawamura & Ikushima, 1993). In addition, it can also be
312 directly emitted by coal combustion and automobile exhaust. The high level of Ph acid in
313 winter in Tianjin aerosols could have been driven by the emission of a large amount of its
314 precursors emitted from coal combustion and/or vehicular exhausts to some extent. In fact, coal
315 consumption, particularly for domestic heating, has been substantially reduced in Tianjin in
316 recent years. However, there are still some localities in northern China, in which coal is the
317 dominant fuel for domestic use. In addition, the air masses were flown from Siberia and pass
318 over Mongolia and most northern Chinese cities in winter (Wang et al., 2018) that should have
319 been enriched with coal combustion emissions. Moreover, the emissions from natural coal and
320 peat fires occurring in Inner Mongolia, China, where the subsurface coal fires are active and
321 one of the more serious fires in the world (Liang et al., 2014), should have been contributed
322 significantly to the atmospheric OA loading in northern China. Interestingly, the relative
323 abundance of Ph acid in Tianjin aerosols (Table 1) is relatively comparable to that reported
324 from Xi'an, China (8.3% in summer and 8.0% in winter), where the emissions from household

325 combustion of coal and plastic burning are significant (Cheng et al., 2013), further supporting
 326 that the contribution from coal combustion to OA is significant over Tianjin.



327 **Figure 3.** Temporal variations of selected diacids (a-c), oxoacids (d,e), and α -dicarbonyls (f) and total
 328 diacids, oxoacids, and α -dicarbonyls (g) in PM_{2.5} from Tianjin, North China during summer and winter, 2016.
 329 Open and close circles and square marks represent day- and night-time, respectively.

330 *t*Ph is derived from industrial emissions and plastic burning (Kawamura & Pavuluri, 2010).
331 The plastic usage is large in China and the municipal solid waste (MSW), which contains
332 significant amount of plastic, is dumped into open landfills in many towns that often set to fire
333 by residents. The concentration of *t*Ph in Tianjin aerosols was higher in winter by a factor of
334 2 than that (48.70 ng m⁻³) reported in Beijing (Zhao et al., 2018) and Chennai, India (range,
335 7.60-168 ng m⁻³; ave. 45.0 ng m⁻³ in winter and 61.3 ng m⁻³ in summer), where MSW that
336 contains significant amount of plastics burning is common (Kawamura & Pavuluri, 2010).
337 Furthermore, the relative abundance of *t*Ph acid in wintertime Tianjin aerosols (Table 1) found
338 to be much higher than that (~4%) reported from Xi'an, China, although it is comparable in
339 summertime (Cheng et al., 2013). Such comparisons with the literature indicate that the plastic
340 burning is an important source of OA over the Tianjin region.

341 Generally, the measured unsaturated diacids, except for M and F (not shown here),
342 showed higher levels in daytime than in nighttime in summer, although the variations were not
343 significant particularly in the case of *t*Ph acid (Fig. 3c). In winter, mM and *t*Ph also did not
344 show a decrease in winter daytime. However, Ph acid showed high abundance in daytime than
345 in nighttime (Fig. 3c). This result implies that either the input of anthropogenic precursors
346 should be large and/or their secondary formation should be more intensive in daytime in Tianjin.

347 3.2.3 Oxoacids and α -dicarbonyls

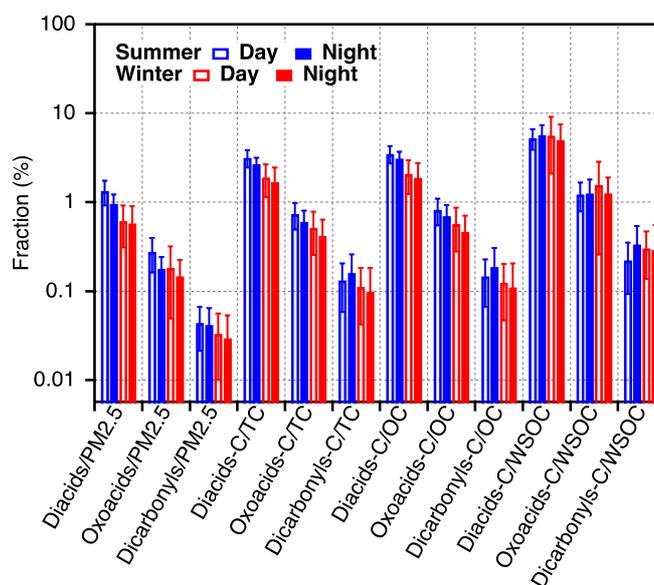
348 Concentrations of ω -oxoacids, Pyr and α -dicarbonyls were found to be higher by a factor
349 of ~3 in winter than those in summer (Table 1). ω C₂ acid was found to be the most abundant
350 oxoacids followed by Pyr and ω C₄, respectively. The second most abundance of Pyr is different
351 from that in New Delhi, where ω C₄ was the second most abundant oxoacids (Miyazaki et al.,
352 2009), and that in Tokyo as well, where the Pyr was most abundant oxoacid species (Kawamura
353 & Yasui, 2005). ω C₂ accounted for 28% and 35% of total oxoacids in Tianjin aerosols in
354 summer and winter, respectively, with a wide range of concentrations ranging from 6.07 to 400
355 ng m⁻³ (ave. 24.2 ng m⁻³ in summer and 118.1 ng m⁻³ in winter) that are higher by a factor of
356 ~2 than that reported in Hong Kong roadside aerosols (18.5 ng m⁻³ and 43.2 ng m⁻³, respectively)
357 (Ho et al., 2006). In contrast, Pyr and ω C₄ were 27% and 19%, respectively, in summer, which
358 are higher than that (25% and 16%, respectively) in winter samples (Table 1). Interestingly,
359 total dicarbonyls also showed higher level in winter than in summer. mGly was more abundant
360 than Gly in both summer and winter.

361 Most of oxoacids and α -dicarbonyls showed relatively high abundance in daytime
362 compared to that in nighttime in winter, whereas in summer, mGly was significantly higher in
363 nighttime (Fig. 3d-f). Gly is largely derived by oxidation of aromatic hydrocarbons, although
364 it can be derived from biogenic and marine emissions for some extent. Therefore, it can be
365 inferred that mGly was produced at night by oxidation of isoprene emitted from terrestrial
366 plants and/or might have extensively transformed to other compounds (e.g., ω C₂) by enhanced
367 photochemical oxidation (Kawamura et al., 1996) during daytime.

368 However, total diacids, oxoacids and α -dicarbonyls showed a clear diurnal variations with
 369 higher levels in daytime in both summer and winter seasons (Fig. 3g), implying that the in-situ
 370 photochemical production was always significant in the Tianjin atmosphere.

371 3.3 Mass Fractions in PM_{2.5}, TC, OC and WSOC

372 The mass fractions of total diacids, oxoacids and α -dicarbonyls in PM_{2.5} and those of their
 373 carbon contents (C) in TC, OC and WSOC in summer and winter are showed in Fig. 4. The
 374 mass fractions of diacids-C in TC and WSOC in Tianjin aerosols together with those reported
 375 from different locale over the world are given in Table 2. Although the concentrations of most
 376 of the diacids and related compounds were higher in winter (Table 1), their fractions in PM_{2.5}
 377 were exactly the opposite; that is, higher in summer (Fig. 4). On average, total diacids
 378 accounted for 0.60% in PM_{2.5} in winter, whereas in summer, it was almost doubled (1.15%) to
 379 that in winter, while the mass fractions of total oxoacids were 0.17% and 0.23%, respectively.
 380 Total α -dicarbonyls were accounted for a very minor (0.04% and 0.03%, respectively) fraction
 381 in PM_{2.5}, which is likely because the α -dicarbonyls largely present in the gas phase.



382 **Figure 4.** Mass ratios of total diacids, oxoacids, and α -dicarbonyls to PM_{2.5} and their carbon contents (C) to
 383 total carbon (TC), organic carbon (OC) and water-soluble OC (WSOC) in the PM_{2.5} from Tianjin, North
 384 China.

385 Total diacids-C accounted for 2.01% to 4.59% (ave. 2.93%) in TC, 2.31-4.97% (3.31%) in
 386 OC in Tianjin PM_{2.5} in summer and 0.55-3.87% (1.79%) and 0.63-4.46% (1.98%), respectively,
 387 in winter. Such seasonal differences clearly indicate that the secondary formation and
 388 transformations of diacids were significantly higher in summer compared to that in winter. The
 389 fractions of oxoacids-C and α -dicarbonyls-C in both OC and TC were less than 1% (Fig. 4),
 390 but they were higher in summer compared to that in winter, which again support our finding
 391 that the aging of OA was more intensive in summer than in winter. In fact, with the enhanced
 392 aging of aerosols, diacids-C/TC ratios will increase because diacids are mainly produced in the

393 atmosphere from photochemical oxidation of precursors, including oxoacids and α -dicarbonyls.
 394 The average contribution of total diacids-C to TC in Tianjin in summer is much higher than
 395 that reported in urban aerosols from Chennai, India, and Tokyo and Sapporo, Japan as well as
 396 in the marine aerosols from the Arctic Ocean in summer (Table 2). However, this ratio is
 397 significantly lower than that reported in the remote marine aerosols from the western north and
 398 central Pacific and the Arctic aerosols from Alert (Table 2), which were considered to be more
 399 aged during the long-range atmospheric transport (Kawamura & Sakaguchi, 1999). These
 400 comparisons suggest that the photochemical production of diacids in the Tianjin atmosphere is
 401 more intensive than in other regions, and they have been subjected for significant aging,
 402 particularly in summer.

403 **Table 2**

404 *Mass Ratios of Total Diacids Carbon to total carbon (TC) and Water-soluble Organic Carbon (WSOC) and*
 405 *Malonic (C₃) to Succinic (C₄) acids in PM_{2.5} from Tianjin and Those at different Locale over the World.*

	Sampling period	Total diacids-C/TC (%)			Total diacids-C/WSOC (%)			C ₃ /C ₄		
		Min	Max	Ave	Min	Max	Ave	Min	Max	Ave
Tianjin, China ^a	July 2016	2.01	4.59	2.93	3.13	9.90	5.46	0.65	3.76	1.06
Tianjin, China ^a	Nov-Dec 2016	0.55	3.87	1.79	1.74	19.9	5.31	0.17	1.22	0.55
Automobile exhaust ^a								0.25	0.44	0.35
Tokyo ^b	Apr 1988-Feb 1989	0.18	1.80	0.95				0.56	2.90	1.60
Chennai, India ^d	Jan-Feb & May 2007	0.40	3.00	1.58	4.00	11.0	5.90			
Gosan, Korea ^e	Apr 2001-Mar 2002	0.80	6.20	3.10						
Western Pacific ^f	Aug-Oct 1992	1.10	4.90	3.20	2.10	14.7	8.20			
WN-Central Pacific ^g	Sept-Dec 1990	1.10	15.8	8.80						
Arctic Ocean ^h	Aug 2009	0.28	2.10	0.87						
Arctic (Alert) ⁱ	Feb-Jun 1991	1.50	9.00	4.00						
Sapporo, Japan ^j	Sept 2009-Oct 2010	1.22	3.03	1.95	3.73	16.3	9.20	1.01	5.18	2.08

406 ^aKawamura and Kaplan, 1987; ^bKawamura and Ikushima, 1993; ^cPavuluri et al., 2010; ^dKawamura et al., 2004; ^eSempere and Kawamura,
 407 2003; ^fKawamura and Sakaguchi, 1999; ^gKawamura et al., 2012; ^hKawamura et al., 2010; ⁱPavuluri et al., 2018; ^jthis study.

408 However, the fraction of diacids-C in WSOC was similar in both the seasons, although
 409 the range is quite broad in winter (Fig. 4). On the other hand, there was no clear diurnal trend
 410 in the fractions of total diacids-C to TC and WSOC. In fact, WSOC (as well as OC and EC)
 411 was increased from summer to winter by a factor of ~3 (Wang et al., 2018) and the
 412 concentrations of total diacids were also higher by a factor of ~2 in winter than that in summer
 413 (Table 1) and thus, their mass ratios have become almost similar in both the seasons. It indicates
 414 that the secondary production of diacids in the Tianjin atmosphere was intensive in winter as
 415 well, but the extent of secondary oxidation and/or transformations organics in winter were not
 416 as intensive as that in summer. Alternatively, the development of inversion layer might result
 417 in accumulation of pollutants including diacids.

418 In summer, temporal trends of total α -dicarbonyls to TC, OC and WSOC were different
 419 from diacids and oxoacids (not shown here). The α -dicarbonyls-C fraction in TC was relatively
 420 constant, except for few cases, whereas that in OC showed a diurnal variation, which is
 421 opposite to that of total diacids-C/OC in early summer. It is likely because the α -dicarbonyls
 422 are first-generation species while the diacids and oxoacids are produced on further oxidation
 423 of the α -dicarbonyls. Such trends demonstrate that the OA over Tianjin was significantly aged
 424 during the long-range atmospheric transport. Fractions of α -dicarbonyls-C in TC ranged from
 425 0.00 to 0.49% (ave. 0.11%) in summer and 0.01-0.38% (0.11%) in winter. They are similar to

426 those Mt .Tai (ave: 0.14%) (Kawamura et al., 2013), but higher than that reported in (ave.
427 0.017%) reported from Arctic Ocean aerosols (Kawamura et al., 2012) and Chennai (0.03%)
428 on the southeast coast of India (Pavuluri et al., 2010). Fractions of α -dicarbonyls-C in WSOC
429 were 0.28% and 0.30% in summer and winter, respectively, and did not show any significant
430 seasonal variation, although their concentrations were increased by a factor of 3 from the
431 summer to winter.

432 3.4 Implications for Origins and Secondary Processes

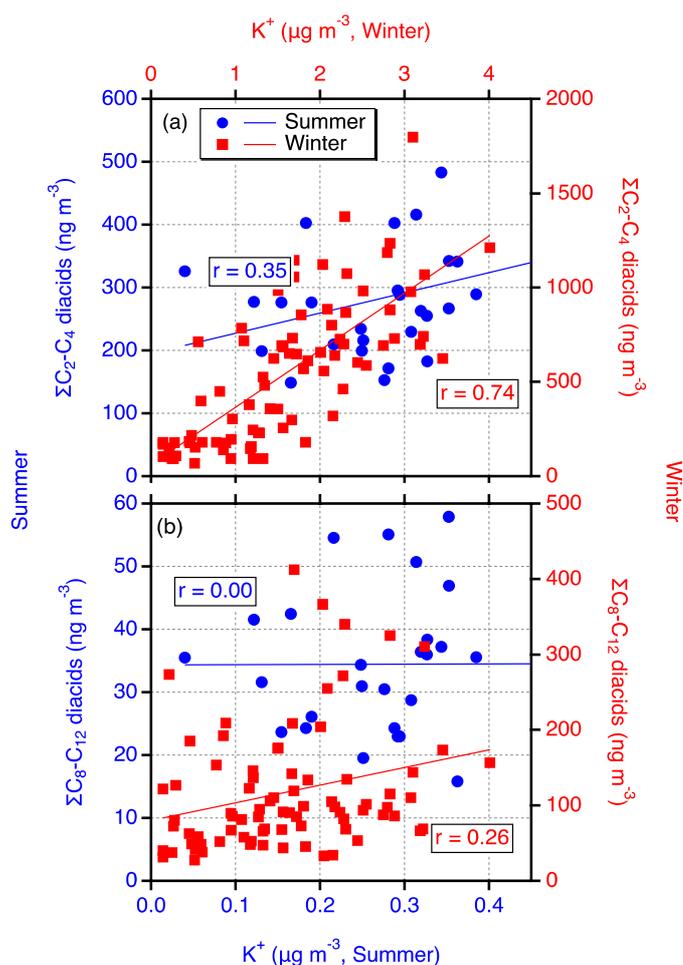
433 3.4.1 Fossil Fuel Combustion and Biomass Burning

434 It has been well established that C₆ diacid and Ph acid are produced by photochemical
435 oxidation of cyclic alkenes (Hatakeyama et al., 1987) and aromatic hydrocarbons (e.g.,
436 naphthalene) of anthropogenic origin (Kawamura & Ikushima, 1993). Whereas C₉ diacid is
437 produced by photochemical oxidation of biogenic unsaturated fatty acids that have a double
438 bond at C-9 position such as oleic acid (Kawamura & Gagosian, 1987). Therefore, the mass
439 ratios of C₆ and Ph acids to C₉ acid have been considered as proxies to evaluate the relative
440 contributions of OA from anthropogenic and biogenic sources (Kawamura et al., 2012).
441 Although average mass ratio of C₆ to C₉ in Tianjin aerosols was almost stable (~0.75) in both
442 the seasons, the average Ph/C₉ (3.65) in winter was significantly higher than that (2.27) in
443 summer. C₆/C₉ ratios in Tianjin are comparable to those reported from 14 cities of China in
444 both winter (ave. 0.62) and summer (0.89) and from Tokyo (0.72) whereas, the Ph/C₉ ratios
445 are comparable to those (3.74) reported from 14 cities of China in winter and lower in summer
446 (4.16) (Ho et al., 2007; Kawamura & Ikushima, 1993). However, both C₆/C₉ and Ph/C₉ ratios
447 are much lower than those reported from Los Angeles (7.4 and 8.0, respectively) (Kawamura
448 & Kaplan, 1987). These results and comparisons suggest that relative contribution of OA from
449 anthropogenic emissions to Tianjin aerosol is similar to that in most of other megacities in
450 China, especially in winter.

451 Kawamura and Kaplan (1987) reported that Ph/C₆ ratio (6.58) in diesel fueled automobile
452 exhaust is higher by a factor of 3 than that in the gasoline fueled automobile exhaust (2.05). In
453 Tianjin aerosols, average Ph/C₆ ratios were 5.02 (range 1.31-11.0) in winter and 3.38 (0.26-
454 7.15) in summer. In addition, these ratios are comparable or slightly higher than those reported
455 from Chennai, India (2.92), where the influence of anthropogenic emissions are significant,
456 although the biomass burning was considered to be a dominant source (Pavuluri et al., 2010).
457 These indicate that the combustion of diesel fuel should be one of the major sources of OA in
458 Tianjin. In fact, gasoline fuel is a common type of fuel for bus and private vehicles in China.
459 Therefore, such high Ph/C₆ ratios indicate that other fossil fuel such as coal combustion might
460 be a significant source of OA rather than gasoline fuel combustion in the Tianjin region.

461 However, as discussed earlier, the concentrations of long-chain diacids including C₉
462 diacid were higher in winter than in summer, indicating the possible enhanced contribution of
463 OA from biomass burning in winter. To confirm such possibility, as shown in Fig. 5, we
464 examined the relations of the sums of short-chain (Σ C₂-C₄) and long-chain (Σ C₈-C₁₂) diacids
465 with potassium ion (K⁺), a tracer for biomass burning (Andreae, 1983). Interestingly, the Σ C₂-

466 C₄ showed a linear relation with K⁺, although the correlation is weak in summer and strong in winter (Fig. 5), suggesting that the short-chain diacids are significantly derived from biomass
 467 burning emissions in both the seasons, particularly in winter. Similarly, the Σ C₈-C₁₂ showed a
 468 linear relation with K⁺ in winter, although the correlation is weak due to few exceptional data
 469 points, but no relation appeared between them in summer (Fig. 5), suggesting that the
 470 contribution of long-chain diacids from biomass burning was significant in winter. In fact, the
 471 loading of K⁺ in Tianjin PM_{2.5} was higher by a factor of ~8 in winter than that in summer,
 472 confirming that the contribution of biomass burning to the PM_{2.5} was highly significant in
 473 winter compared to that in summer.
 474



475 **Figure 5.** Scatter plots between the sums of (a) short-chain (Σ C₂-C₄) and (b) long-chain (Σ C₈-C₁₂) diacids
 476 and potassium ion (K⁺) in PM_{2.5} from Tianjin, North China in summer and winter.

477 3.4.2 Photochemical Secondary Formation and Aging

478 It has been established that C₃ and C₄ diacids are emitted from primary sources such as
 479 fossil fuel combustion and biomass burning, however, the relative contribution of the former
 480 is small compared to the latter, because the C₃ is unstable at high temperatures (Kawamura &
 481 Ikushima, 1993). However, C₃ can be produced by photochemical breakdown of C₄ diacid
 482 (Charbouillot et al., 2012; Kawamura et al., 1996; Pavuluri et al., 2015). Hence, C₃/C₄ ratio has
 483 been considered as a measure to assess the extent of aging of OA in the atmosphere (Aggarwal

484 & Kawamura, 2008; Kawamura & Ikushima, 1993). The C₃/C₄ ratios in Tianjin PM_{2.5} were
485 found to be always higher in summer than those reported for vehicular emissions, whereas in
486 winter, their lower ends were comparable to those of the vehicular emissions (Table 2).
487 Furthermore, the average C₃/C₄ in summer was more than twice to that in winter and
488 comparable to those reported from Tokyo but lower than that reported from Sapporo, Japan
489 and from the remote Pacific, which are considered to be aged (Kawamura & Sakaguchi, 1999).
490 Such results and comparisons suggest that the diacids and related compounds in Tianjin PM_{2.5}
491 are largely produced by secondary formation, particularly in summer but not subjected for more
492 aging, whereas in winter, the emissions from fossil fuel combustion should have also been
493 contributed significantly.

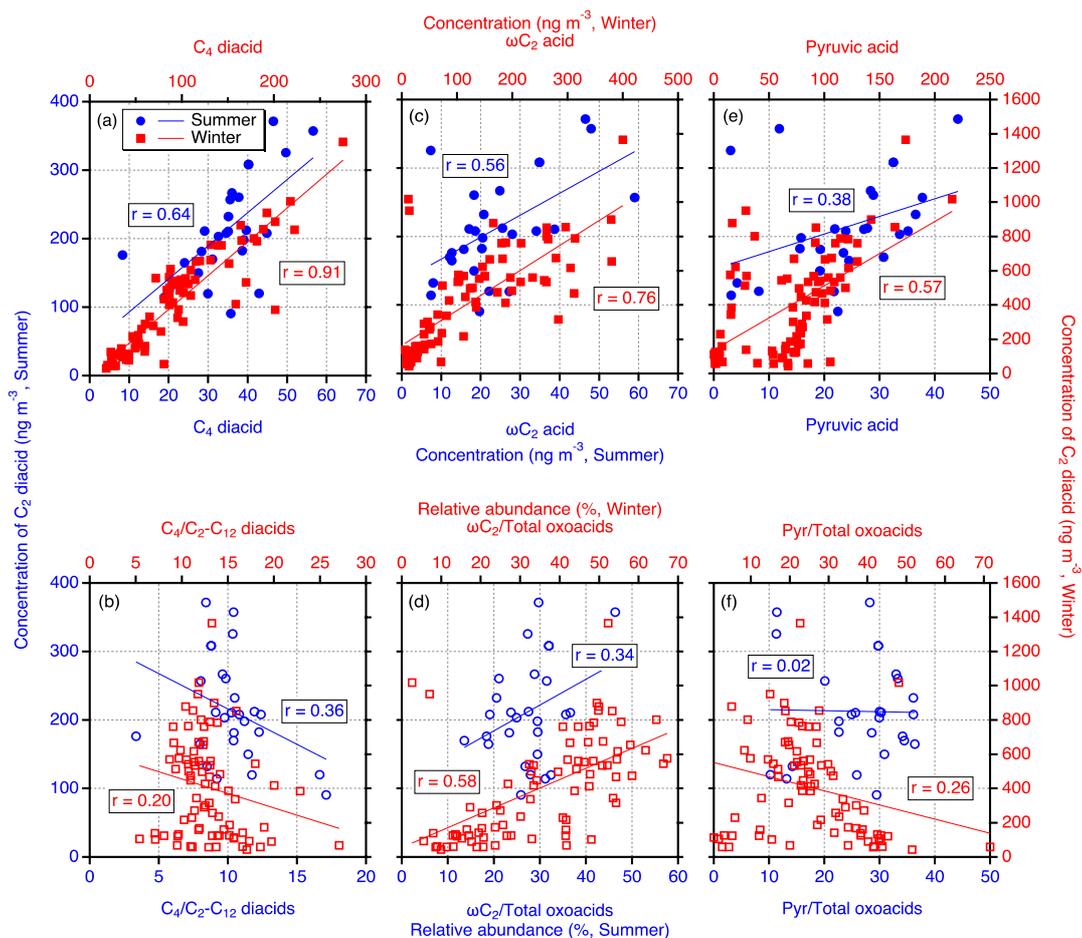
494 However, the C₃/C₄ ratios found to be higher in daytime (ave. 1.03; range 0.64-1.40) than
495 that (0.88; 0.73-1.10) in nighttime in summer, but such diurnal variations were not appeared in
496 winter. In addition, the C₃/C₄ showed a significant correlation ($r = 0.59$, $p < 0.05$) with ambient
497 temperature in daytime. These results indicate that photochemical aging was intensive under
498 high ambient temperatures and strong solar radiation in daytime in the Tianjin urban
499 atmosphere that promotes the transformation of C₄ to C₃ diacid. Moreover, the C₆/C₉ mass
500 ratios presented a relatively clear diurnal trends with higher values in daytime (ave. 0.64) than
501 those in nighttime (0.59) in summer. Similar diurnal variations were appeared in the case of
502 Ph/C₉ as well. They further support that the aging (breakdown of C₉ to its lower homologues)
503 was more intensive during daytime than in nighttime.

504 In contrast, averaged mass ratio of M to F acid did not show a significant difference
505 between summer (1.43 ± 0.81) and winter (1.68 ± 0.90). In fact, the transformation of M acid
506 (*cis*-form) to F acid (*trans*-form) increases with aging under strong solar radiation and hence,
507 the M/F ratio is decreased in the more aged OA (Kundu et al., 2010a; Kundu et al., 2010b).
508 Furthermore, the M/F ratios in Tianjin PM_{2.5} are higher by a factor of ~3 than those (ave. 0.56)
509 reported in marine aerosols from the North Pacific (Kawamura & Sakaguchi, 1999) and Chichi-
510 jima island (Mochida, 2003), which have been considered as more aged, implying that the OA
511 in Tianjin PM_{2.5} are relatively less aged and significantly derived from the sources at a regional
512 scale. However, the relative abundance of C₂ diacid (C₂%) to total diacids, which can be used
513 as a measure of the extent of OA aging, was accounted for up to 63% in summer with relatively
514 high abundance (49%) in nighttime than in daytime (47%). In winter, C₂% was significantly
515 lower than that in summer and did not show any difference between day- and night-time (35.6%
516 and 36%, respectively). Such high C₂% implies that the Tianjin OA were significantly aged
517 and the contributions from long-range transported air masses cannot be precluded.

518 3.4.3 Possible Secondary Formation in Aqueous Phase

519 C₂ diacid is produced from photochemical breakdown of its higher homologues: C₃ and
520 C₄ diacids, and oxoacids: ωC₂ and Pyr acids, that derived from α-dicarbonyls in aqueous phase
521 (Carlton et al., 2007; Ervens, 2004; Kawamura & Ikushima, 1993; Kawamura et al., 1996;
522 Warneck, 2003). Recently, Pavuluri et al. (2015) found that the production of C₄ diacid is much
523 higher compared to all other species including C₂ diacid and its production is increased with
524 increasing UV irradiation time in aqueous aerosols until the precursor compounds are

525 completely oxidized. Thereafter, the concentration of C₄ diacid starts to decrease with UV
 526 irradiation due to photochemical breakdown into its lower homologues: C₃ and C₂ diacids
 527 (Pavuluri et al., 2015). Kawamura et al. (2012) found high abundance of C₄ diacid than C₂
 528 diacid in some of marine aerosol samples collected under overcast conditions with fog or brume
 529 events over the Arctic Ocean. However, they have been attributed the low abundance of the C₂
 530 diacid for its degradation in aqueous phase, preferably in presence of water-soluble iron. In
 531 contrast, Miyazaki et al. (2009) found high abundance of C₂ diacid in nighttime, which is
 532 consistent with the increase in SO₄²⁻ loading, and attributed to enhanced production in aqueous
 533 phase.

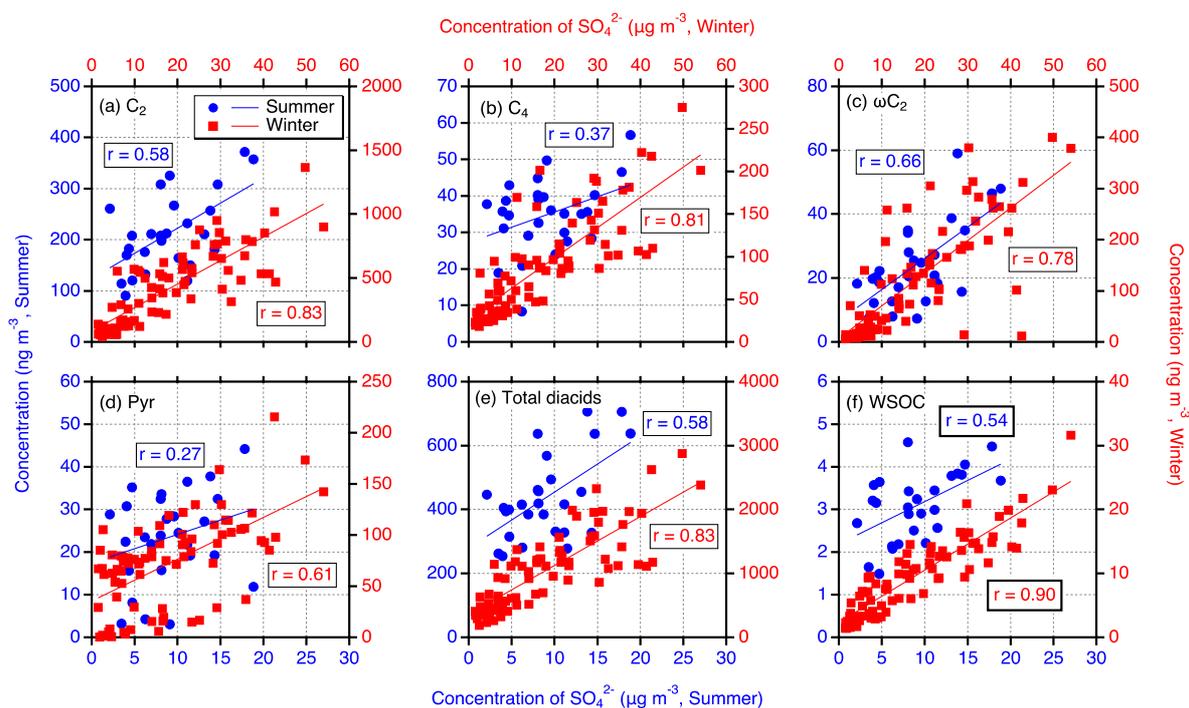


534 **Figure 6.** Scatter plots between concentration of C₂ diacid and the concentrations of C₄ diacid (a), ω C₂ acid
 535 (b), and pyruvic acid (c), and relative abundance of C₄ diacid in total normal saturated (C₂-C₁₂) diacids (d),
 536 the relative abundances of ω C₂ acid (e) and pyruvic acid (f) in total oxoacids in PM_{2.5} from Tianjin, North
 537 China in summer and winter. See Table 1 for abbreviations of symbols.

538 Though the average concentrations of C₂ and C₃ diacids were increased by only about 2.0
 539 and 1.4 folds, respectively, those of C₄ diacid and Pyr acid were increased by ~3 times while
 540 that of ω C₂ was increased by a factor of 5 from summer to winter in Tianjin PM_{2.5} (Table 1).
 541 Furthermore, the relative abundances of C₂ and C₃ diacids to total diacids were decreased by a
 542 factor of about 1.4 and 2, respectively, from summer to winter, whereas that of C₄ diacid to
 543 total diacids and those of ω C₂ and Pyr acids to total oxoacids remained almost same in both
 544 the seasons (Table 1). Such higher levels and abundances of C₄, ω C₂ and Pyr acids in winter

545 compared to those of C₂ and C₃ diacids imply that the secondary formation of diacids and
 546 related compounds and/or degradation of the C₂ and C₃ diacids in aqueous phase might be
 547 significant in the Tianjin atmosphere, particularly in winter, although we do not preclude such
 548 possibility in summer as well.

549 It has been well established that C₄ (and C₃) diacids, ωC₂ acid and Pyr (*via* ωC₂ acid) acid
 550 that are mainly produced from their precursors in aqueous phase can easily transformed into
 551 C₂ diacid upon further oxidation in the aqueous phase (Carlton et al., 2007; Ervens, 2004;
 552 Kawamura et al., 1996; Pavuluri et al., 2015; Warneck, 2003). Hence, the relations of C₄, ωC₂
 553 and Pyr with C₂ diacid could provide better insights to assess the role of aqueous phase
 554 reactions in the formation of secondary organic aerosols in the Tianjin atmosphere. As shown
 555 in Fig. 6a,c,e, concentrations of C₂ diacid showed a very good, good and modern linear relation
 556 with those of C₄ (and C₃, not shown here), ωC₂ acid and Pyr, respectively, in winter and
 557 moderate relations in summer. In fact, the relative humidity was high up to 80% in winter,
 558 which could promote the aqueous phase oxidation reactions and thus played a significant role
 559 in SOA generation in winter in the Tianjin atmosphere compared to that in summer. On the
 560 other hand, as discussed earlier, the aging of aerosols should have been more intensive in
 561 summer under strong solar radiation and high ambient temperatures that could have promoted
 562 the enhanced photochemical transformation of C₄ (and C₃), ωC₂ and Pyr to an ultimate product,
 563 C₂ diacid, rather than simultaneous formation of all the species, in summer.



564 **Figure 7.** Scatter plots between concentrations of (a) C₂ diacid, (b) C₄ diacid, (c) ωC₂ acid,
 565 (e) total diacids and (f) water-soluble organic carbon (WSOC) in PM_{2.5} from Tianjin, North China in summer
 566 and winter. See Table 1 for abbreviations of symbols. WSOC data is obtained from Wang et al. (2018).

567 Furthermore, concentrations of C₂ diacid showed an inverse relation with the relative
 568 abundance of C₄ diacid (C₄%) to the total normal (ΣC₂-C₁₂) diacids as well as with that of Pyr

569 to total oxoacids in both the seasons, although the coefficients were weak (Fig. 6b,f).
570 Interestingly, the correlation coefficient between C₂ and C₄% was slightly higher in summer
571 than that in winter, whereas that between C₂ and Pyr% was higher in winter than in summer
572 (Fig. 6b,f). In contrast, C₂ diacid showed a linear relation with the relative abundance of ωC₂
573 acid (ωC₂%) to total oxoacids in both the seasons, however, the correlation coefficient between
574 them was higher in winter than that in summer (Fig. 6d). These results imply that the formation
575 of C₂ diacid by photochemical breakdown of C₄ (and C₃) diacids should have been dominated
576 in summer whereas in winter, the C₂ diacid should have been mainly produced *via* ωC₂ acid in
577 aqueous phase. The linear relation between C₂ and ωC₂% indicates the formation of the ωC₂
578 acid from its precursors must be more effective than its transformation to C₂ diacid in aqueous
579 phase. Of course, the degradation of C₂ diacid could also be effective in aqueous phase, if
580 sufficient amount of water-soluble iron available in the liquid aerosol, that can also results the
581 positive relation between C₂ and ωC₂%.

582 Yu et al. (2005) found very good correlation between SO₄₂₋ and C₂ diacid in atmospheric
583 aerosols from several locations over East Asia and interpreted that the C₂ diacid is highly
584 produced in aqueous aerosols and its loading is increased with the increasing level of the SO₄₂₋.
585 As shown in Fig. 7, C₂ diacid as well as C₄, ωC₂ and Pyr acids, total diacids and total oxoacids
586 (not shown here) showed linear relations with SO₄₂₋ with high and moderate (weak in the case
587 of C₄ and Pyr acids) correlation coefficients in winter and summer, respectively. The
588 correlation coefficient between total oxoacids and SO₄₂₋ was 0.50 in summer and 0.81 in winter.
589 Interestingly, WSOC also showed very strong and moderate linear relationship with the SO₄₂₋
590 in winter and summer, respectively (Fig. 7f). These linear relations imply that *in-situ* secondary
591 formation of OA including diacids and related compounds in aqueous phase is significant in
592 both the seasons but more intensive and thus the OA are less aged in winter. In summer,
593 particularly the poor correlation between C₄ and Pyr acids, which are mostly first generation
594 species in aqueous phase, and SO₄₂₋ indicates that the aging of OA generated at local scale
595 under strong solar radiation as well as transported from distant source regions in North China
596 was significant. Moreover, the strong correlation of WSOC with the SO₄₂₋ indicate that the
597 water-soluble OA loading is increased with the increasing in SO₄₂₋ levels, probably due to the
598 enhancement in oxidation of OA species in aqueous phase under acidic conditions in the
599 Tianjin atmosphere. Therefore, it is highly necessary to further reduce the emission of oxidant
600 species such as SO₂ and NO_x and thus, the reduction of H₂SO₄ and HNO₃ and subsequently the
601 water-soluble OA in North China.

602 4 Conclusions

603 Diacids and related compounds measured in PM_{2.5} samples collected on day- and night-
604 time basis in summer and winter 2016 from Tianjin, North China showed the high abundance
605 of C₂ diacid followed by ωC₂, Ph and *t*Ph acids, respectively. C₄ diacid was the second most
606 abundant diacids followed by C₃ diacid, while Pyr was the second most abundant oxoacids. All
607 diacid, oxoacid and α-dicarbonyl species, except for kC₃ and kC₇, showed a high loading in
608 winter than in summer, but their mass fractions in PM_{2.5} were exactly the opposite; higher in
609 summer than in winter. On average, total diacids-C accounted for 2.93% in TC and 3.31% in

610 OC in summer and 1.79% and 1.98%, respectively, in winter. Although the diurnal pattern was
611 not systematic, on average, most of the species showed a diurnal pattern. Diacids, oxoacids and
612 α -dicarbonyls are relatively abundant in the Tianjin atmosphere compared to those reported
613 from most of other urban localities over China in winter. Mass ratios of C₆/C₉, Ph/C₉ and Ph/C₆
614 diacids and their comparison with the literature together with the linear relations of sum of
615 short-chain (Σ C₂-C₄) and long-chain (Σ C₈-C₁₂) diacids with K₊ indicated that anthropogenic
616 emissions, mainly coal combustion, and biomass burning emissions are the major sources in
617 Tianjin region and their contributions are significantly enhanced in winter. The mass ratios of
618 C₃/C₄ and M/F as and the relative abundance of C₂ diacid (C₂%) to total diacids suggested that
619 the diacids and related compounds in Tianjin PM_{2.5} are largely produced by in-situ secondary
620 formation but the aging of OA and the contributions from long-range transported air masses
621 cannot be precluded, particularly in summer. The linear relations between concentrations of C₂
622 diacid those of C₄, ω C₂ and Pyr acids and with the relative abundance of C₄ diacid (C₄%) to
623 the total normal (Σ C₂-C₁₂) diacids, and that of ω C₂ and Pyr to total oxoacids as well as with
624 SO₄₂₋ implied that the in-situ secondary formation of OA including diacids and related
625 compounds in aqueous phase is significant in both the seasons but more intensive and thus the
626 OA are less aged in winter. In summer, the aging of OA generated at local scale as well as
627 transported from distant source regions was significant in North China. The strong correlation
628 of WSOC with the SO₄₂₋ indicated that the water-soluble OA loading is increased with the
629 increasing in SO₄₂₋ levels and need to reduce the emission of oxidants such as SO₂ and NO_x to
630 control the water-soluble OA loading in North China.

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651 **References**

- 652 Aggarwal, S. G., & Kawamura, K. (2008). Molecular distributions and stable carbon isotopic
653 compositions of dicarboxylic acids and related compounds in aerosols from Sapporo, Japan:
654 Implications for photochemical aging during long-range atmospheric transport. *Journal of*
655 *Geophysical Research*, 113.
- 656 Albrecht, B. A. (1989). Aerosols, Cloud Microphysics, and Fractional Cloudiness. *Science*, 245(4923),
657 1227-1230. <Go to ISI>://WOS:A1989AP68700033
- 658 Andreae, M. O. (1983). Soot carbon and excess fine potassium: long-range transport of combustion-
659 derived aerosols. *Science*, 220, 1148-1151.
- 660 Andreae, M. O., & Crutzen, P. J. (1997). Atmospheric aerosols: Biogeochemical sources and role in
661 atmospheric chemistry. *Science*, 276(5315), 1052-1058.
- 662 Asa-Awuku, A., Moore, R. H., Nenes, A., Bahreini, R., Holloway, J. S., Brock, C. A., et al. (2011).
663 Airborne cloud condensation nuclei measurements during the 2006 Texas Air Quality Study.
664 *Journal of Geophysical Research-Atmospheres*, 116. <Go to ISI>://WOS:000291315900003
- 665 Baltensperger, U., Dommen, J., Alfarra, R., Duplissy, J., Gaeggeler, K., Metzger, A., et al. (2008).
666 Combined determination of the chemical composition and of health effects of secondary organic
667 aerosols: The POLYSOA project. *Journal of Aerosol Medicine and Pulmonary Drug Delivery*,
668 21(1), 145-154. <Go to ISI>://WOS:000257859100014
- 669 Bian, H., Han, S. Q., Tie, X. X., Sun, M. L., & Liu, A. X. (2007). Evidence of impact of aerosols on
670 surface ozone concentration in Tianjin, China. *Atmospheric Environment*, 41(22), 4672-4681. <Go
671 to ISI>://WOS:000247769100009
- 672 Cao, J. J., Lee, S. C., Chow, J. C., Watson, J. G., Ho, K. F., Zhang, R. J., et al. (2007). Spatial and
673 seasonal distributions of carbonaceous aerosols over China. *Journal of Geophysical Research*,
674 112(D22).
- 675 Carlton, A. G., Turpin, B. J., Altieri, K. E., Seitzinger, S., Reff, A., Lim, H.-J., & Ervens, B. (2007).
676 Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation
677 experiments. *Atmospheric Environment*, 41(35), 7588-7602.
- 678 Carmichael, G. R., Adhikary, B., Kulkarni, S., D'Allura, A., Tang, Y., Streets, D., et al. (2009). Asian
679 Aerosols: Current and Year 2030 Distributions and Implications to Human Health and Regional
680 Climate Change. *Environmental Science & Technology*, 43(15), 5811-5817.
- 681 Charbouillot, T., Gorini, S., Voyer, G., Parazols, M., Brigante, M., Deguillaume, L., et al. (2012).
682 Mechanism of carboxylic acid photooxidation in atmospheric aqueous phase: Formation, fate and
683 reactivity. *Atmospheric Environment*, 56, 1-8.
- 684 Cheng, C. L., Wang, G. H., Zhou, B. H., Meng, J. J., Li, J. J., Cao, J. J., & Xiao, S. (2013). Comparison
685 of dicarboxylic acids and related compounds in aerosol samples collected in Xi'an, China during
686 haze and clean periods. *Atmospheric Environment*, 81, 443-449. <Go to
687 ISI>://WOS:000329377600048
- 688 Ervens, B. (2004). A modeling study of aqueous production of dicarboxylic acids: 1. Chemical
689 pathways and speciated organic mass production. *Journal of Geophysical Research*, 109(D15).
- 690 Facchini, M. C., Mircea, M., Fuzzi, S., & Charlson, R. J. (1999). Cloud albedo enhancement by surface-
691 active organic solutes in growing droplets. *Nature*, 401(6750), 257-259. <Go to
692 ISI>://WOS:000082678400047

693 Folkers, M., Mentel, T. F., & Wahner, A. (2003). Influence of an organic coating on the reactivity of
694 aqueous aerosols probed by the heterogeneous hydrolysis of N₂O₅. *Geophysical Research Letters*,
695 30(12). <Go to ISI>://WOS:000184577400006

696 Fu, P., Kawamura, K., Okuzawa, K., Aggarwal, S. G., Wang, G., Kanaya, Y., & Wang, Z. (2008).
697 Organic molecular compositions and temporal variations of summertime mountain aerosols over
698 Mt. Tai, North China Plain. *Journal of Geophysical Research*, 113(D19).

699 Fu, P., Kawamura, K., Usukura, K., & Miura, K. (2013). Dicarboxylic acids, ketocarboxylic acids and
700 glyoxal in the marine aerosols collected during a round-the-world cruise. *Marine Chemistry*, 148,
701 22-32. <Go to ISI>://WOS:000314441600003

702 Fuzzi, S., Andreae, M. O., Huebert, B. J., Kulmala, M., Bond, T. C., Boy, M., et al. (2006). Critical
703 assessment of the current state of scientific knowledge, terminology, and research needs concerning
704 the role of organic aerosols in the atmosphere, climate, and global change. *Atmospheric Chemistry
705 and Physics*, 6, 2017-2038. <Go to ISI>://WOS:000238152100001

706 Grosjean, D., & Fung, K. (1984). Hydrocarbons and carbonyls in Los Angeles air. *Journal of Air
707 Pollution and Control Association*, 34, 537-543.

708 Hatakeyama, S., Ohno, M., Weng, J. H., Takagi, H., & Akimoto, H. (1987). Mechanism for the
709 Formation of Gaseous and Particulate Products from Ozone-Cycloalkene Reactions in Air.
710 *Environmental Science and Technology*, 21, 52-57.

711 Ho, K. F., Cao, J. J., Lee, S. C., Kawamura, K., Zhang, R. J., Chow, J. C., & Watson, J. G. (2007).
712 Dicarboxylic acids, ketocarboxylic acids, and dicarbonyls in the urban atmosphere of China.
713 *Journal of Geophysical Research*, 112(D22).

714 Ho, K. F., Ho, S. S. H., Lee, S. C., Kawamura, K., Zou, S. C., Cao, J. J., & Xu, H. M. (2011). Summer
715 and winter variations of dicarboxylic acids, fatty acids and benzoic acid in PM_{2.5} in Pearl Delta
716 River Region, China. *Atmospheric Chemistry and Physics*, 11(5), 2197-2208. <Go to
717 ISI>://WOS:000288368900022

718 Ho, K. F., Lee, S. C., Cao, J. J., Kawamura, K., Watanabe, T., Cheng, Y., & Chow, J. C. (2006).
719 Dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban roadside area of Hong Kong.
720 *Atmospheric Environment*, 40(17), 3030-3040. <Go to ISI>://WOS:000237904700003

721 Huang, R. J., Zhang, Y. L., Bozzetti, C., Ho, K. F., Cao, J. J., Han, Y. M., et al. (2014). High secondary
722 aerosol contribution to particulate pollution during haze events in China. *Nature*, 514(7521), 218-
723 222. <Go to ISI>://WOS:000342663100040

724 Kawamura, K., & Bikkina, S. (2016). A review of dicarboxylic acids and related compounds in
725 atmospheric aerosols: Molecular distributions, sources and transformation. *Atmospheric Research*,
726 170, 140-160. <Go to ISI>://WOS:000368866500014

727 Kawamura, K., & Gagosian, R. B. (1987). Implications of w-oxocarboxylic acids in the remote marine
728 atmosphere for photo-oxidation of unsaturated fatty acids. *Nature*, 325, 330-332.

729 Kawamura, K., & Ikushima, K. (1993). Seasonal changes in the distribution of dicarboxylic acids in the
730 urban atmosphere. *Environmental Science & Technology*, 27, 2227-2235.

731 Kawamura, K., & Kaplan, I. R. (1987). Motor exhaust emissions as a primary source for dicarboxylic
732 acids in Los Angeles ambient air. *Environmental Science and Technology*, 21(1), 105-110.

- 733 Kawamura, K., Kasukabe, H., & Barrie, L. A. (1996). Source and reaction pathways of dicarboxylic
734 acids, ketoacids and dicarbonyls in Arctic aerosols: One year of observations. *Atmospheric*
735 *Environment*, 30(10/11), 1709-1722.
- 736 Kawamura, K., Kasukabe, H., & Barrie, L. A. (2010). Secondary formation of water-soluble organic
737 acids and alpha-dicarbonyls and their contributions to total carbon and water-soluble organic carbon:
738 Photochemical aging of organic aerosols in the Arctic spring. *Journal of Geophysical Research-*
739 *Atmospheres*, 115. <Go to ISI>://WOS:000284219100007
- 740 Kawamura, K., Kobayashi, M., Tsubonuma, N., Mochida, M., Watanabe, T., & Lee, M. (2004). Organic
741 and inorganic compositions of marine aerosols from East Asia: Seasonal variations of water-soluble
742 dicarboxylic acids, major ions, total carbon and nitrogen, and stable C and N isotopic composition.
743 In J. L. R.J. Hill, Z. Aizenshtat, M.J. Baedecker, G. Claypool, & M. G. a. K. P. R. Eganhouse (Eds.),
744 *Geochemical Investigations in Earth and Space Science: A Tribute to Isaac R. Kaplan* (Vol. 9, pp.
745 243-265): The Geochemical Society, Publication.
- 746 Kawamura, K., Ono, K., Tachibana, E., Charrière, B., & Sempéré, R. (2012). Distributions of low
747 molecular weight dicarboxylic acids, ketoacids and α -dicarbonyls in the marine aerosols collected
748 over the Arctic Ocean during late summer. *Biogeosciences*, 9(11), 4725-4737.
- 749 Kawamura, K., & Pavuluri, C. M. (2010). New Directions: Need for better understanding of plastic
750 waste burning as inferred from high abundance of terephthalic acid in South Asian aerosols.
751 *Atmospheric Environment*, 44(39), 5320-5321. [http://www.scopus.com/inward/record.url?eid=2-](http://www.scopus.com/inward/record.url?eid=2-s2.0-78049315366&partnerID=MN8TOARS)
752 [s2.0-78049315366&partnerID=MN8TOARS](http://www.scopus.com/inward/record.url?eid=2-s2.0-78049315366&partnerID=MN8TOARS)
- 753 Kawamura, K., & Sakaguchi, F. (1999). Molecular distributions of water soluble dicarboxylic acids in
754 marine aerosols over the Pacific Ocean including tropics. *Journal of Geophysical Research:*
755 *Atmospheres*, 104(D3), 3501-3509.
- 756 Kawamura, K., Tachibana, E., Okuzawa, K., Aggarwal, S. G., Kanaya, Y., & Wang, Z. F. (2013). High
757 abundances of water-soluble dicarboxylic acids, ketocarboxylic acids and α -dicarbonyls in the
758 mountaintop aerosols over the North China Plain during wheat burning season. *Atmospheric*
759 *Chemistry and Physics*, 13(16), 8285-8302.
- 760 Kawamura, K., & Yasui, O. (2005). Diurnal changes in the distribution of dicarboxylic acids,
761 ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere. *Atmospheric Environment*,
762 39(10), 1945-1960.
- 763 Kolb, C. E., & Worsnop, D. R. (2012). Chemistry and composition of atmospheric aerosol particles.
764 *Annu Rev Phys Chem*, 63, 471-491. <https://www.ncbi.nlm.nih.gov/pubmed/22404591>
- 765 Kundu, S., Kawamura, K., Andreae, T. W., Hoffer, A., & Andreae, M. O. (2010a). Molecular
766 distributions of dicarboxylic acids, ketocarboxylic acids and alpha-dicarbonyls in biomass burning
767 aerosols: implications for photochemical production and degradation in smoke layers. *Atmospheric*
768 *Chemistry and Physics*, 10(5), 2209-2225. <Go to ISI>://WOS:000275505500009
- 769 Kundu, S., Kawamura, K., & Lee, M. (2010b). Seasonal variations of diacids, ketoacids, and α -
770 dicarbonyls in aerosols at Gosan, Jeju Island, South Korea: Implications for sources, formation, and
771 degradation during long-range transport. *Journal of Geophysical Research*, 115(D19).
- 772 Kunwar, B., & Kawamura, K. (2014). Seasonal distributions and sources of low molecular weight
773 dicarboxylic acids, ω -oxocarboxylic acids, pyruvic acid, α -dicarbonyls and fatty acids in ambient

774 aerosols from subtropical Okinawa in the western Pacific Rim. *Environmental Chemistry*, 11(6),
775 673-689.

776 Liang, Y., Liang, H., & Zhu, S. (2014). Mercury emission from coal seam fire at Wuda, Inner Mongolia,
777 China. *Atmospheric Environment*, 83, 176-184.

778 Meng, H., Xueqiang, L., Chunsheng, Z., Liang, R., & Suqin, H. (2015). Characterization and source
779 apportionment of volatile organic compounds in urban and suburban Tianjin, China. *Advances in*
780 *Atmospheric Sciences*, 32, 439-444.

781 Miyazaki, Y., Aggarwal, S. G., Singh, K., Gupta, P. K., & Kawamura, K. (2009). Dicarboxylic acids
782 and water-soluble organic carbon in aerosols in New Delhi, India, in winter: Characteristics and
783 formation processes. *Journal of Geophysical Research*, 114(D19).

784 Mochida, M. (2003). Spatial distributions of oxygenated organic compounds (dicarboxylic acids, fatty
785 acids, and levoglucosan) in marine aerosols over the western Pacific and off the coast of East Asia:
786 Continental outflow of organic aerosols during the ACE-Asia campaign. *Journal of Geophysical*
787 *Research*, 108(D23).

788 Nakajima, T., Yoon, S.-C., Ramanathan, V., Shi, G.-Y., Takemura, T., Higurashi, A., et al. (2007).
789 Overview of the Atmospheric Brown Cloud East Asian Regional Experiment 2005 and a study of
790 the aerosol direct radiative forcing in east Asia. *Journal of Geophysical Research*, 112.

791 Novakov, T., & Penner, J. E. (1993). Large Contribution of Organic Aerosols to Cloud-Condensation-
792 Nuclei Concentrations. *Nature*, 365(6449), 823-826. <Go to ISI>://WOS:A1993MD95100045

793 Pavuluri, C. M., Kawamura, K., Aggarwal, S. G., & Swaminathan, T. (2011). Characteristics,
794 seasonality and sources of carbonaceous and ionic components in the tropical aerosols from Indian
795 region. *Atmospheric Chemistry and Physics*, 11(15), 8215-8230.

796 Pavuluri, C. M., Kawamura, K., Mihalopoulos, N., & Swaminathan, T. (2015). Laboratory
797 photochemical processing of aqueous aerosols: formation and degradation of dicarboxylic acids,
798 oxocarboxylic acids and α -dicarbonyls. *Atmospheric Chemistry and Physics*, 15(14), 7999-8012.

799 Pavuluri, C. M., Kawamura, K., & Swaminathan, T. (2010). Water-soluble organic carbon, dicarboxylic
800 acids, ketoacids, and α -dicarbonyls in the tropical Indian aerosols. *Journal of Geophysical Research*,
801 115.

802 Prenni, A. J., DeMott, P. J., Kreidenweis, S. M., Sherman, D. E., Russell, L. M., & Ming, Y. (2001).
803 The effects of low molecular weight dicarboxylic acids on cloud formation. *Journal of Physical*
804 *Chemistry A*, 105(50), 11240-11248. <Go to ISI>://WOS:000172945600012

805 Ramanathan, V., Crutzen, P. J., Kiehl, J. T., & Rosenfeld, D. (2001). Aerosols, Climate, and the
806 Hydrological Cycle. *Science*, 294, 2119-2124.

807 Saxena, P., Hildemann, L. M., & McMurry, P. H. (1995). Organics alter hygroscopic behavior of
808 atmospheric particles. *Journal of Geophysical Research*, 100, 18755-18770.

809 Tilgner, A., & Herrmann, H. (2010). Radical-driven carbonyl-to-acid conversion and acid degradation
810 in tropospheric aqueous systems studied by CAPRAM. *Atmospheric Environment*, 44(40), 5415-
811 5422.

812 Twomey, S. (1977). Influence of Pollution on Shortwave Albedo of Clouds. *Journal of the Atmospheric*
813 *Sciences*, 34(7), 1149-1152. <Go to ISI>://WOS:A1977DP78800020

814 Wang, G., Niu, S., Liu, C., & Wang, L. (2002). Identification of dicarboxylic acids and aldehydes of
815 PM10 and PM2.5 aerosols in Nanjing, China. *Atmospheric Environment*, 36, 1941-1950.

816 Wang, G. H., Kawamura, K., Cheng, C. L., Li, J. J., Cao, J. J., Zhang, R. J., et al. (2012). Molecular
817 Distribution and Stable Carbon Isotopic Composition of Dicarboxylic Acids, Ketocarboxylic Acids,
818 and alpha-Dicarbonyls in Size-Resolved Atmospheric Particles From Xi'an City, China.
819 *Environmental Science & Technology*, 46(9), 4783-4791. <Go to ISI>://WOS:000303348800019
820 Wang, G. H., Kawamura, K., Hatakeyama, S., Takami, A., Li, H., & Wang, W. (2007). Aircraft
821 measurement of organic aerosols over China. *Environmental Science & Technology*, 41(9), 3115-
822 3120. <Go to ISI>://WOS:000246371100019
823 Wang, S., Pavuluri, C. M., Ren, L. J., Fu, P. Q., Zhang, Y. L., & Liu, C. Q. (2018). Implications for
824 biomass/coal combustion emissions and secondary formation of carbonaceous aerosols in North
825 China. *Rsc Advances*, 8(66), 38108-38117. <Go to ISI>://WOS:000450902700063
826 Warneck, P. (2003). In-cloud chemistry opens pathway to the formation of oxalic acid in the marine
827 atmosphere. *Atmospheric Environment*, 37, 2423-2427.
828 Yang, L., Ray, M. B., & Yu, L. E. (2008). Photooxidation of dicarboxylic acids—Part II: Kinetics,
829 intermediates and field observations. *Atmospheric Environment*, 42(5), 868-880.
830 Yu, J. Z., Huang, X.-F., Xu, J., & Hu, M. (2005). When aerosol sulfate goes up, so does oxalate:
831 Implication for the formation mechanisms of oxalate. *Environmental Science & Technology*, 39(1),
832 128-133.
833 Zhang, X. Y., Wang, Y. Q., Niu, T., Zhang, X. C., Gong, S. L., Zhang, Y. M., & Sun, J. Y. (2012).
834 Atmospheric aerosol compositions in China: spatial/temporal variability, chemical signature,
835 regional haze distribution and comparisons with global aerosols. *Atmospheric Chemistry and*
836 *Physics*, 12(2), 779-799.
837 Zhang, Y.-L., Kawamura, K., Fu, P. Q., Boreddy, S. K. R., Watanabe, T., Hatakeyama, S., et al. (2016).
838 Aircraft observations of water-soluble dicarboxylic acids in the aerosols over China. *Atmospheric*
839 *Chemistry and Physics*, 16(10), 6407-6419.
840 Zhao, W. Y., Kawamura, K., Yue, S. Y., Wei, L. F., Ren, H., Yan, Y., et al. (2018). Molecular
841 distribution and compound-specific stable carbon isotopic composition of dicarboxylic acids,
842 oxocarboxylic acids and alpha-dicarbonyls in PM_{2.5} from Beijing, China. *Atmospheric Chemistry*
843 *and Physics*, 18(4), 2749-2767. <Go to ISI>://WOS:000426244400001
844