



1 **Molecular distribution and compound-specific stable**
2 **carbon isotopic composition of dicarboxylic acids,**
3 **oxocarboxylic acids, and α -dicarbonyls in PM_{2.5} from**
4 **Beijing, China**

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25 Abstract

26 This study investigates the seasonal variation, molecular distribution and stable carbon
27 isotopic composition of diacids, oxocarboxylic acids and α -dicarbonyls to better understand
28 the sources and formation processes of fine aerosols ($PM_{2.5}$) in Beijing. The concentrations of
29 total dicarboxylic acids varied from 110 to 2580 $ng\ m^{-3}$, whereas oxoacids (9.50–353 $ng\ m^{-3}$)
30 and dicarbonyls (1.50–85.9 $ng\ m^{-3}$) were less abundant. Oxalic acid was found to be the most
31 abundant individual species, followed by succinic acid or occasionally by terephthalic acid
32 (tPh), a plastic burning tracer. Ambient concentrations of phthalic acid ($37.9\pm 27.3\ ng\ m^{-3}$)
33 and tPh ($48.7\pm 51.1\ ng\ m^{-3}$) are larger in winter than in other seasons, illustrating that fossil
34 fuel combustion and plastic waste incineration contribute more significantly to wintertime
35 aerosols. The year-round mass concentration ratios of malonic acid to succinic acid (C_3/C_4)
36 are relatively by comparison with those in other urban aerosols and remote marine aerosols,
37 most of which are less than or equal to unity in Beijing; thus, the degree of photochemical
38 formation of diacids in Beijing is insignificant. Moreover, positive correlations of some
39 oxocarboxylic acids and α -dicarbonyls with $nss-K^+$, a tracer for biomass burning, suggest
40 biogenic combustion activities accounting for a large contribution of these organic acids and
41 related precursors. The mean $\delta^{13}C$ value of succinic acid is highest among all species with
42 values of $-17.1\pm 3.9\%$ (winter) and $-17.1\pm 2.0\%$ (spring), while malonic acid is less enriched
43 in ^{13}C than others in autumn ($-17.6\pm 4.6\%$) and summer ($-18.7\pm 4.0\%$). The $\delta^{13}C$ values of
44 major species in the Beijing aerosols are generally lower with a wider range than those in
45 downwind regions in the western North Pacific, which indicates that Beijing has diverse
46 emission sources with weak photooxidation. Thus, our study demonstrates that in addition to
47 photochemical oxidation, high abundances of diacids, oxocarboxylic acids and α -dicarbonyls
48 in Beijing are largely associated with anthropogenic primary emissions, such as biomass
49 burning, fossil fuel combustion, and plastic burning.

50



51 1 Introduction

52 Haze pollution events are largely characterized by high levels of fine aerosol particles ($PM_{2.5}$)
53 and have received considerable public attention in China during the past few years (Cao,
54 2012; Zhang et al., 2014; Zhao et al., 2013). $PM_{2.5}$ influences air quality, visibility, human
55 health, radiative forcing and global climates (Ulbrich et al., 2009; Sun et al., 2013) and is
56 heavily involved with organic aerosols, making up 20–50% of aerosol mass (Kanakidou et al.,
57 2005) and no less than 90% in tropical forest areas (Falkovich et al., 2005). Interestingly,
58 large quantities of organic aerosols are water-soluble, resulting in corresponding proportion
59 from 20% to 75% of total carbon mass in particles, which originate from incomplete
60 combustion activities (biomass burning: 45–75%, fossil fuel burning: 20–60%) (Pathak et al.,
61 2011; Falkovich et al., 2005). Due to their hygroscopic properties, water-soluble organic
62 aerosols (WSOA) act as an important role in global climate change by influencing solar
63 radiation (Facchini et al., 1999; Saxena et al., 1995).

64 Homologues series of diacids, oxoacids and α -dicarbonyls comprise a major portion of
65 WSOA (Kawamura and Ikushima, 1993; Miyazaki et al., 2009). Owing to the existence of
66 two carboxyl groups, diacids are less volatile and highly water soluble, and they play an
67 important role in acting as CCN to affect the earth's radiative balance. (Kanakidou et al.,
68 2005; Andreae and Rosenfeld, 2008). They are widely present in urban (Ho et al., 2007),
69 rural (Kundu et al., 2010a), marine (Fu et al., 2013), and the Arctic atmospheres (Kawamura
70 et al., 1996a). Concentrations of total diacids contribute approximately 1–3% to the total
71 carbon mass in urban regions and more than 10% in remote marine atmospheres (Kawamura
72 and Ikushima, 1993; Kawamura et al., 1996b; Kawamura et al., 1996c). Diacids, ketoacids
73 and α -dicarbonyls not only can be directly released from primary emissions like biomass
74 burning (Turnhouse, 1987; Destevou et al., 1998; Schauer et al., 2001; Kundu et al., 2010a),
75 meal cooking (Rogge et al., 1991; Schauer et al., 1999; Zhao et al., 2007), fossil fuel burning
76 (Kawamura and Kaplan, 1987; Rogge et al., 1993) along with motor vehicles (Kawamura and
77 Kaplan, 1987; Donnelly et al., 1988), but also are largely produced by photooxidation
78 reactions during atmospheric transport (Kawamura and Yasui, 2005; Kundu et al., 2010b).



79 Breakdown of relatively long carbon-chain diacids and other related precursors is also one of
80 the key sources of low carbon-numbered diacids in the atmosphere (Agarwal et al., 2010).

81 Realizing the physical and chemical characteristics of organic matters is vital for determining
82 the source regions and elucidating the mechanism of evolution of air pollution events.
83 Various measurements have been employed for closer acquaintances of the sources,
84 transformation and long-distance transport of organic compounds, including studies on sugars,
85 unsaturated fatty acids, *n*-alkanes and *n*-alcohol, along with aromatic hydrocarbons
86 (Kawamura and Gagosian, 1987; Kawamura et al., 1996a). Zhang et al. (2010) conducted
87 field observations of dicarboxylic acids and pinene oxidation products with a model analysis
88 of the temperature dependencies of emissions, gas-particle partitioning, and chemical
89 reactions. Furthermore, the analyses of stable carbon isotope ratios of water-soluble organic
90 acids can be effectively applied to assessing the photochemical aging of aerosol samples in
91 atmosphere (Kawamura and Watanabe, 2004; Wang and Kawamura, 2006c). With this
92 approach, it is possible to differentiate between the impacts of local sources and long-range
93 transported air masses.

94 Beijing, the capital of China, is located on the northwest rim of the North China Plain and is
95 embraced with industrialized areas from the southwest to the east. Emissions from local and
96 regional sources potentially undergo photochemical processes in the course of transport by
97 means of prevalent winds, which influence the atmospheric visibility and quality in Beijing
98 (Xia et al., 2007). Several studies have reported that the source strength of aerosols in Beijing
99 is characterized by fossil fuel combustion in winter, whereas it is characterized by secondary
100 aerosol formation in summer (Lin et al., 2009; Sun et al., 2015; Wang et al., 2006). Ji et al.
101 (2016) observed increasing photochemical activity in autumn and winter and noted biomass
102 burning as a substantial pollution factor in Beijing. In addition to the studies on long-term
103 observations of organic aerosols, specific haze pollution episodes occurring in Beijing have
104 been investigated. For example, Huang et al. (2014) concluded that in comparison with
105 secondary sources, primary emissions contributed slightly less to fine particles in haze events
106 at urban locations in China, including Beijing, using both molecular markers and radiocarbon
107 (^{14}C) measurements. To ascertain the influential factors for air quality in Beijing, two studies



108 demonstrated that besides vehicle emissions, oxidation pathways of organic species is also
109 critical (Ho et al., 2010; Ho et al., 2015). Although such studies have focused on the
110 characterization of organic aerosols in Beijing at a molecular level, long-term analyses of low
111 molecular weight (LMW) dicarboxylic acids, oxoacids and α -dicarbonyls with their stable
112 carbon isotopic compositions have not been investigated.

113 To better understand the sources, photochemical processes, and seasonal distributions of
114 organic aerosols in Beijing, $PM_{2.5}$ samples were collected from September 2013 to July 2014.
115 These samples were analyzed for organic carbon (OC), elemental carbon (EC), water-soluble
116 organic carbon (WSOC) and inorganic ions. In addition to reporting the concentrations and
117 seasonal variations of LMW dicarboxylic acids, oxoacids and α -dicarbonyls, we investigated
118 the seasonal trends of stable carbon isotopic compositions of these water-soluble organic
119 acids. Using these measurements, the contribution of primary emissions, long-range transport,
120 as well as photochemical production ways of organic matters in Beijing were examined. The
121 effects of air masses on aerosol compositions and formation mechanisms are also discussed.

122

123 **2 Experimental section**

124 **2.1 $PM_{2.5}$ sampling**

125 The sampling site is situated on the rooftop of a building (8 meters above ground level) in the
126 Institute of Atmospheric Physics (39°58'28''N, 116°22'16''E), which is considered as a
127 representative urban site in Beijing (Sun et al., 2012). $PM_{2.5}$ samples were collected onto
128 pre-heated (450°C, 6 hours) quartz-fiber filters (Pallflex) by using a high-volume air sampler
129 (TISCH, USA) at an airflow rate of 1.0 m³/min from September 2013 to July 2014 (n=65).
130 Field blanks were prepared before, during and after the campaign by putting the
131 pre-combusted filter onto the sampler for a few minutes without pumping. Beijing is
132 surrounded by Hebei Province and Tianjin Municipality with intensely developed industries
133 (Xia et al., 2007), so the atmospheric visibility and quality in Beijing are sometimes seriously
134 deteriorated owing to the substantial primary aerosols from these areas.



135 **2.2 Analytical procedures**

136 Aerosol samples were analyzed for diacids and related compounds using a method reported
137 previously (Kawamura, 1993; Kawamura and Ikushima, 1993). In brief, water-soluble
138 organic acids were obtained from ultrasonic extraction for small discs of PM_{2.5} samples
139 merged in Milli-Q water for 3 times. Then, the sample extractions were concentrated into
140 dryness and further reacted with 14% BF₃/*n*-butanol. Finally, the derivatized extracts were
141 dissolved in *n*-hexane and analyzed by a split/splitless Agilent 6980 GC/FID equipped with
142 an HP-5 column (0.2 mm × 25 m, 0.5 μm film thickness). The field blank filters were also
143 used same procedures to analyze. Concentrations of the target organic acids in this study were
144 corrected for the field blanks. Furthermore, recoveries of major organic acids of this method
145 were better than 85%.

146 **2.3 Measurement of isotopic compounds**

147 Determination of stable carbon isotope ratio ($\delta^{13}\text{C}$) values for LMW diacids and related
148 constituents relative to Pee Dee Belemnite (PDB) were used the technique set up previously
149 (Kawamura and Watanabe, 2004). In short, $\delta^{13}\text{C}$ values of the derivatized dibutyl esters or
150 dibutoxy acetals, measured using GC (HP6890)/isotope ratio mass spectrometer (irMS), were
151 calculated for diacids, ketoacids and α -dicarbonyls. Every aerosol sample was analyzed for
152 several times to make sure that the differences for major diacids in $\delta^{13}\text{C}$ below 1‰ in general.
153 But as to few compounds, the analysis differences were less than 2‰.

154 **2.4 Inorganic ions, WSOC, OC and EC measurements**

155 A part of each filter was extracted with 20 ml of Milli-Q water under ultrasonication for 30
156 minutes and passed through a filter head of 0.22 μm nominal pore size (PVDF, Merck
157 Millipore Ltd). Ion chromatography (ICS-2100) was used to determine the concentrations of
158 cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺). The separation of cations was accomplished by
159 using an IonPac CS 12A (4×250 mm) analytical column, with an eluent flow rate of 1.0
160 ml/min. Another ICS-2100 system was used to measure the concentrations of anions (F⁻, Cl⁻,
161 NO₃⁻, and SO₄²⁻). The separation of anions was accomplished using an IonPac AS11-HC
162 analytical column. The eluent was 25.0 mM KOH at a flow rate of 1.0 ml/min. The anions



163 and cations were analyzed separately after the extraction solution was divided into two paths.
164 For the WSOC measurement, 3.14 cm² of each filter was extracted by Milli-Q water (20 ml).
165 After 15 min sonication, the extraction was measured by Shimadzu TOC-V CPH Total
166 Carbon Analyzer (Aggarwal and Kawamura, 2008). OC and EC were determined by using
167 thermal optical reflectance (TOR) following the Interagency Monitoring of Protected Visual
168 Environments (IMPROVE) protocol on a DRI Model 2001 Thermal/Optical Carbon Analyzer
169 (Chow et al., 2005). The limit of detection (LOD) for the carbon analysis was 0.8 µgC cm⁻²
170 for OC and 0.4 µgC cm⁻² for EC, with a precision of greater than 10% for total carbon (TC).
171 The concentrations of inorganic ions, WSOC and OC/EC reported here are all corrected for
172 the field blanks.

173 2.5 Air mass backward trajectories

174 To better evaluate the influences of air masses from different origins on organic aerosols in
175 Beijing, 5-day backward trajectory analyses with fire spots were performed for each sample
176 from the sampling site at a height of 500 m (a.s.l.) by using the Hybrid Single-Particle
177 Lagrangian Integrated Trajectory (HYSPPLIT4) mode (Rolph, 2011, 2003). And fire spot data
178 were downloaded from the MODIS website
179 (<https://firms.modaps.eosdis.nasa.gov/download/request.php>). The backward trajectories
180 were assorted into several major classifications on the basis of prevalent winds direction, as
181 given below in this study (Fig. 1).

182

183 3 Results and discussion

184 3.1 Molecular distribution

185 Table 1 summarizes the seasonal concentrations of LMW diacids (C₂–C₁₂), oxocarboxylic
186 acids (ωC₂–ωC₉, pyruvic acid), and α-dicarbonyls (C₂–C₃) in PM_{2.5} particles in Beijing.
187 Oxalic acid (30.8–1760 ng m⁻³, average 288 ng m⁻³) was the predominant individual diacid,
188 showing a peak in autumn and a minimum in winter, whereas its relative abundances (0.39–
189 0.58, average 0.52) to total measured species exhibited a maximal and a minimal ratio in



190 summer and wintertime, respectively (Table 3). The predominance of C₂ found in this study
191 was coincident with the results of terrestrial and marine particles in previous studies
192 (Kawamura and Yasui, 2005; Ho et al., 2007; Pavuluri et al., 2010; Fu et al., 2013). Among
193 ω-oxocarboxylic acids (ωC₂–ωC₉), glyoxylic acid (ωC₂) was detected as the dominant
194 oxoacid.

195 Either succinic acid (C₄) or occasionally tPh was the second most abundant compound,
196 followed by ωC₂ in cold seasons (autumn and winter) or malonic acid (C₃) in warm seasons
197 (spring and summer). Total diacids showed the largest abundance in autumn, followed by
198 spring, whereas total oxoacids and α-dicarbonyls both displayed higher levels in cold seasons,
199 especially in autumn (Table 1). The concentrations of single dicarboxylic acid reduced along
200 with the increase of carbon numbers, but in the range of longer-chain diacids (C₆–C₁₂), adipic
201 (C₆) and azelaic (C₉) acids showed more abundances than other species in the atmosphere
202 throughout the year (Fig. 2).

203 3.2 Seasonal variations

204 Seasonal trends of homologues series of diacids and other main species presented three
205 different patterns. The first type, such as oxalic, malonic, succinic, adipic acids and
206 methylglyoxal (MeGly), showed maximum concentrations in autumn with relatively high
207 abundances in late spring to early summer. The second type showed maximum concentrations
208 in cold seasons (autumn, winter): phthalic, terephthalic and glyoxylic acid peaked in winter,
209 while C₉, glyoxal (Gly), methylmaleic (mM), maleic (M) and fumaric (F) acids peaked in
210 autumn. For the third type, concentrations of methylmalonic (iC₄) and 2-methylglutaric (iC₆)
211 acids were almost constant throughout the sampling year. These three seasonal trends
212 indicated different emission sources of the compounds and their precursors and evolution
213 processes of organic aerosols in the atmosphere.

214 Total concentrations of diacids showed a wide range (110–2580 ng m⁻³) with an average
215 maximum (763 ng m⁻³) and minimum (366 ng m⁻³) in autumn and winter, respectively. These
216 values were comparable to those in Tanzania, East Africa (wet season: 329 ng m⁻³; dry
217 season: 548 ng m⁻³ in PM_{2.5}) (Mkoma and Kawamura, 2013), slightly lower than those in



218 Tokyo, Japan (726 ng m^{-3} in June, 682 ng m^{-3} in July, and 438 ng m^{-3} in November)
219 (Kawamura and Yasui, 2005), and Gosan, Jeju Island in Korea (735 ng m^{-3} in spring, 784 ng
220 m^{-3} in summer, 525 ng m^{-3} in autumn, and 500 ng m^{-3} in winter) (Kundu et al., 2010a). The
221 comparisons of the diacids in Beijing with those in other urban cities are presented in Table
222 2.

223 Daily variations of diacids and other major organic acids are given in Figure 3. Oxalic acid
224 has been recognized as the end product that is associated with atmospheric chain reactions of
225 organic species with oxidants (Kawamura and Sakaguchi, 1999). C_2 can be generated in
226 abundant quantities by vehicular emissions (Kawamura and Kaplan, 1987; Donnelly et al.,
227 1988), biomass burning activities (Turnhouse, 1987; Destevou et al., 1998; Schauer et al.,
228 2001), fossil fuel combustion (Rogge et al., 1993), and photo-oxidation of volatile organic
229 compounds and other precursors transported from long distance (Kawamura and Yasui, 2005;
230 Kundu et al., 2010b). Malonic acid was detected at relatively low concentrations in four
231 sampling periods, with the highest abundances in autumn. The concentrations of C_4 diacid in
232 excess of C_3 diacid implies that primary emissions contributed more to dicarboxylic acids, a
233 typical pattern that is frequently obtained in aerosols emitted from biomass burning
234 (Kawamura et al., 2013), vehicular exhaust (Ho et al., 2010) and fossil fuel combustion (Ho
235 et al., 2007). The diurnal variation tendency of C_2 resembled to that of both C_3 and C_4 , with
236 the trends C_3 and C_4 being almost the same, indicating that these compounds may have
237 similar photochemical oxidation pathways or emission sources in the atmosphere.

238 In addition to shorter-chain diacids (C_2 – C_4), azelaic acid (C_9) had the highest concentration
239 among the saturated diacids in all seasons (Table 1). C_9 , a photochemical oxidation product
240 of unsaturated fatty acids derived from natural biogenic sources such as terrestrial higher
241 plants and sea-to-air emission of marine organics, as well as anthropogenic emissions
242 including biomass burnings (Kawamura and Gagosian, 1987). Under favorable atmospheric
243 conditions, photooxidation of biogenic unsaturated fatty acids to C_9 with oxidants, such as O_3 ,
244 OH and HO_2 , are inclined to occur in air (Stephanou and Stratigakis, 1993). Additionally, tire
245 wear debris and traffic exhaust also make contributions to the abundances of LMW fatty
246 acids like $\text{C}_{18:0}$ in atmosphere (Rogge et al., 1993).



247 Azelaic acid was observed in abundance throughout the whole sampling period, while the
248 monthly mean ratios of C₉ to total diacids (C₉/Tot) ranged from 0.05 to 0.09, with the highest
249 values in winter (Table 3). Kawamura and Kaplan (1987) reported that C₉ can be detected in
250 motor exhaust and may originate from the oxidation of corresponding hydrocarbons,
251 suggesting that dicarboxylic acids are combustion products of normal alkanes in fuels. A
252 great deal of chloride in wintertime Beijing is linked to increased emissions of coal
253 incineration, particularly under stagnant meteorological conditions that facilitate the
254 formation of particle-phase ammonium chloride (Sun et al., 2013). Azelaic acid correlated
255 well with K⁺ ($0.3 \leq r^2 \leq 0.4$) and Cl⁻ ($0.4 \leq r^2 \leq 0.5$) in cold seasons (Fig. S1), indicating that
256 substantial amounts of C₉ may be stemmed from the local and surrounding combustion
257 activities in Beijing.

258 Abundances of both Ph and tPh are higher in cold seasons than in warm seasons. We found
259 Ph to be the fourth most abundant species in winter ($37.9 \pm 27.2 \text{ ng m}^{-3}$) and summer
260 ($24.9 \pm 8.2 \text{ ng m}^{-3}$). Concentration ranges of Ph (7.6–98.5 ng m⁻³, mean: 31.7 ng m⁻³) in cold
261 seasons were larger than those (0.08–7.47 ng m⁻³, mean: 1.76 ng m⁻³) from Gosan, Jeju Island
262 (Kundu et al., 2010b), but were obviously lower than these (53–278 ng m⁻³, mean: 150 ng m⁻³)
263 in urban Xi'an (Cheng et al., 2013). Phthalic acid is mainly formed via photochemical
264 pathways of naphthalene, and can also be directly released into air by fossil fuel burning and
265 the incomplete combustion of aromatic hydrocarbons in automobile emissions. A great
266 amount of naphthalene obtained in Beijing is an important raw material for the substantial
267 formation of phthalic acid (Liu et al., 2007). Thus, high concentrations of Ph in PM_{2.5}
268 demonstrate that vehicle emissions are one of the major pollution sources in Beijing.

269 Terephthalic acid (tPh), the second highest abundant diacid in winter ($48.7 \pm 41.1 \text{ ng m}^{-3}$),
270 showed a pattern in contrast to a previous study that reported Ph as the second most abundant
271 compound (Ho et al., 2010). Terephthalic acid is directly emitted from plastic wastes
272 incinerations in ambient air (Simoneit et al., 2005; Kawamura and Pavuluri, 2010). High
273 concentration peaks of tPh observed in winter indicate substantial plastic waste incineration.
274 Another phthalic isomer, isophthalic acid (iPh), was also detected in the samples;
275 concentrations of this isomer had seasonal patterns similar to those of Ph and tPh throughout



276 the year. However, the concentrations of iPh were the lowest among the isomers.

277 Oxocarboxylic acids, which are understood as the intermediate products of the oxidation of
278 mono-carboxylic acids, can further be photo-chemically oxidized to form diacids.
279 Concentrations of all ketoacids varied from 9.50 to 353 ng m⁻³ during sampling periods with
280 a maximum (73.3±76.3 ng m⁻³) in autumn and a minimum (46.5±26.8 ng m⁻³) in summer.
281 More abundant oxoacids, other than ωC₇ and ωC₈, in cold seasons (autumn and winter) might
282 be attributed to accumulation under stagnant meteorological conditions. Their concentrations
283 were higher than those in aerosols from Tanzania (60.0±19.0 ng m⁻³ and 31.0±18.0 ng m⁻³ in
284 PM_{2.5} during dry and wet seasons, respectively) (Mkoma and Kawamura, 2013) but much
285 lower than these detected in Mangshan, a rural site in Beijing (159 ng m⁻³ in daytime, 97.9 ng
286 m⁻³ in nighttime) (He et al., 2014).

287 Glyoxylic acid (ωC₂) is measured as the most abundant oxoacid, followed by pyruvic (Pyr)
288 and 4-oxobutanoic (ωC₄) acids. All of them are important intermediates in photooxidation
289 processes for the production of low carbon-numbered diacids such as C₂, C₃ and C₄ diacids
290 (Hatakeyama et al., 1987). ωC₂ and Pyr are more abundant in cold seasons (Table 1) with
291 similar seasonal patterns (Fig. 3 g–h) and have good correlations with K⁺ (Fig. S2) in the
292 whole sampling period. ωC₂ and Pyr only correlated well with Cl⁻ (Fig. S3) in cold seasons.
293 These connections demonstrate that ωC₂ and Pyr originated from common combustion
294 emissions or similar secondary formation pathways. 9-Oxononanoic acid (ωC₉),
295 photochemically generated from unsaturated fatty acids (Kawamura and Gagosian, 1987),
296 showed larger concentrations in autumn and winter. This concentration trend was consistent
297 with that of azelaic acid. Additionally, a lower thermal inversion layer, less precipitation and
298 a slower wind speed can enhance the accumulation of organic compounds.

299 Total concentrations of α-dicarbonyls varied with a wide range (1.50–85.9 ng m⁻³) and were
300 relatively more abundant in cold seasons (25.1±28.1 ng m⁻³ in autumn, 15.5±15.9 ng m⁻³ in
301 winter). And the average seasonal concentrations are larger than those at Gosan, Jeju island in
302 South Korea (Kundu et al., 2010b). Two α-dicarbonyls (glyoxal and methylglyoxal) are
303 semi-volatile gaseous organic precursors produced by oxidation of isoprene (Zimmermann
304 and Poppe, 1996), monoterpenes (Fick et al., 2004) and other biogenic volatile organic



305 compounds (VOCs) (Ervens et al., 2004) and anthropogenic aromatic hydrocarbons (e.g.,
306 benzene and toluene) (Volkamer et al., 2001). Both carbonyls can form less volatile organic
307 polar acids including Pyr and ω C₂ in subsequent oxidation processes, which are key
308 intermediates to produce oxalic acid (C₂). Glyoxal (Gly) and methylglyoxal (MeGly)
309 correlated well with nss-K⁺ (Gly: $0.3 \leq r^2 \leq 0.9$, MeGly: $0.3 \leq r^2 \leq 0.9$) throughout the whole
310 year (Fig. S2), whereas Gly and MeGly showed good relations with Cl⁻ (Gly: $0.3 \leq r^2 \leq 0.8$,
311 $0.4 \leq r^2 \leq 0.8$) in autumn, winter and summer (Fig. S3). Concentrations of these two
312 carbonyls are largely affected by biogenic precursors (e.g., isoprene and monoterpenes)
313 emitted from vegetation and biomass burning activities during entire sampling periods in
314 addition to coal burning and motor exhaust (aromatic hydrocarbons). Low temperature is
315 favorable for the adsorption and condensation of gaseous organic species on existing particles
316 in cold seasons.

317 3.3 Correlation analysis and seasonal variations of concentration ratios

318 The ratio of oxalic acid to total diacids (C₂/Tot) has been applied to estimate the relative
319 contribution of secondary fraction to atmospheric aerosols during long-range transport.
320 Typically, higher mass concentration ratios are associated with more aged aerosols
321 (Kawamura and Sakaguchi, 1999). As for water-soluble organic acids in this paper, the ratios
322 of C₂/Tot were the lowest in winter (0.39 ± 0.05) (Table 3), indicating that wintertime organic
323 aerosols may be less aged (Fig. 4a). Because PM_{2.5} particles mainly originate from motor
324 vehicles, fossil fuel and biomass combustion activities from local regions in winter, the aging
325 process might occur during atmospheric transport. In contrast, C₂/Tot ratios are similar in the
326 other three seasons (Table 3). In total, the seasonal mean values of C₂/Tot in this study were
327 lower than those in Central Himalayan in winter (0.8 ± 0.04) owing to the aging of organic
328 compounds occurring in the northerly wind and were close to those in summer (0.5 ± 0.01) due
329 to increased temperature and high wind in the Central Himalayas (Hegde and Kawamura,
330 2012). Thus, the ratios of C₂/Tot and this seasonal trend indicate that the photochemical
331 formation of dicarboxylic acids is insignificant in urban Beijing.

332 Two pathways for the generation of C₂, C₃ and C₄ diacids in air were reported by Kawamura



333 et al. (1996a). On the one hand, C_4 diacid can be generated via the photooxidation of
334 unsaturated fatty acids from terrestrial higher plants and domestic cooking over continental
335 lands, as well as from phytoplankton emissions over the remote marine regions (Kawamura
336 and Sakaguchi, 1999), and subsequently be oxidized to form C_3 and C_2 diacids (Kawamura
337 and Ikushima, 1993). Typically, C_2/Tot ($C_2\%$) showed strong correlations with C_2/C_4 in all
338 four seasons (Fig. S4), indicating the significance of photooxidation pathways of biogenic
339 unsaturated fatty acids. On the other hand, aromatic hydrocarbons may be oxidized to
340 produce Gly and ωC_2 , which are intermediates in the formation of C_2 (Kawamura and
341 Ikushima, 1993). Biogenic and anthropogenic VOCs (e.g., isoprene) can react with oxidants
342 to generate Gly and MeGly in the gas phase. Hydrated α -dicarbonyls can ultimately produce
343 C_2 via the photochemical oxidation of Pyr and ωC_2 as intermediates (Lim et al., 2005),
344 whereas C_3 and C_4 diacids cannot be produced in this way.

345 In this study, we examined the seasonal variations of concentration ratios such as C_2/Pyr ,
346 $C_2/\omega C_2$ and C_2/Gly to evaluate the oxidation strength of related precursors to the formation of
347 C_2 . Relative high ratios of C_2/Pyr , $C_2/\omega C_2$ and C_2/Gly were observed in sampling seasons
348 except winter (Fig. 4c-e), but their values were much lower than those detected in particulate
349 matters at Gosan, Jeju Island (Kundu et al., 2010b), where the aerosols were relatively aged
350 during long-range transport. Figure S4 shows that strong relationships between $C_2/\omega C_2$,
351 C_2/Pyr and C_2/Tot (%) only existed in summer. No correlation was observed between C_2/Gly
352 and C_2/Tot (%). A negative correlation between $C_2/\omega C_2$ and C_2/Tot (%) in summer has never
353 been reported before. These phenomena demonstrate that abundant C_2 , ωC_2 , Pyr, and Gly
354 were emitted directly from biogenic burning emissions, in the studied regions throughout the
355 year (Fig. 1). Only slightly stronger photochemical production of C_2 from Pyr was observed
356 in summer.

357 C_3 diacid can be produced as a result of hydrogen abstracted by OH radicals, followed by
358 decarboxylation processing of C_4 diacid (Kawamura and Ikushima, 1993). The mass
359 concentration ratio of C_3/C_4 is a good indicator for evaluating the contributions of
360 dicarboxylic acids from primary emissions or secondary oxidation production in the
361 atmosphere. Lower C_3/C_4 ratios were detected in vehicular exhaust by Kawamura and



362 Ikushima (1993), ranging from 0.25 to 0.44 with an average of 0.35. Less thermally stable C₃
363 diacid can degrade more preferentially to other species rather than remaining stable during
364 incomplete combustion processes.

365 Figure 4b shows that the C₃/C₄ ratios were relatively larger in the warm seasons (spring &
366 summer). However, the temporal trend of the C₃/C₄ ratios is relatively flat through the
367 sampling year. Most are less than or equal to unity, which is associated with the substantial
368 emissions from motor vehicles (Kawamura and Kaplan, 1987). The relatively low values of
369 the C₃/C₄ ratios caused by motor emissions were also detected in a previous study
370 (Kawamura and Kaplan, 1987). On the contrary, the prolonged secondary oxidation of
371 organic matters leads to C₃/C₄ values much greater than unity (Kawamura and Ikushima,
372 1993; Kawamura and Sakaguchi, 1999). The ratios of C₃/C₄ reported in this study are lower
373 than that (one-year average of 1.49) in urban Tokyo (Kawamura and Ikushima, 1993) and in
374 the remote Pacific Ocean (average 3) (Kawamura and Sakaguchi, 1999), where dicarboxylic
375 acids are largely produced by photooxidation reactions. These results demonstrated that in
376 addition to slightly enhanced atmospheric photochemical reactions in summer, incomplete
377 combustions overwhelmingly contributed to dicarboxylic acids in Beijing.

378 Phthalic acid (Ph) was one of the most abundant compounds during the sampling period. The
379 seasonal trends of phthalic acid to total dicarboxylic acids (Ph/Tot) are shown in Figure 4h.
380 The Ph/Tot ratios in winter were nearly 2–3 times greater than those in spring and autumn.
381 These findings imply that phthalic acid is largely emitted by anthropogenic sources in winter,
382 mainly as a result of intensive fossil fuel combustion. It is worth noting that Ph was abundant
383 in summer when increased ambient temperatures and stronger solar radiation facilitate the
384 transformation of gaseous PAHs (e.g., naphthalene) to produce relatively high levels of Ph.

385 C₆ and Ph are mostly formed via secondary oxidations of anthropogenic cyclic olefins (e.g.,
386 cyclohexene) and aromatic hydrocarbons, respectively, whereas C₉ is a photochemical
387 product of biogenic unsaturated fatty acids (Kawamura and Gagosian, 1987; Kawamura and
388 Ikushima, 1993). Thus, the mass concentration ratios of C₆/C₉ and Ph/C₉ may effectively
389 indicate the source strength of anthropogenic and biogenic emissions to these organic acids.



390 The seasonally averaged ratios of C_6/Tot , C_9/Tot , C_6/C_9 and Ph/C_9 are displayed in Table 3.
391 Mean values of C_6/Tot are constantly low in all four seasons, whereas the seasonal ratios of
392 C_9/Tot are the highest (0.09) in winter and the lowest (0.05) in summer, which result in the
393 lowest value of C_6/C_9 ratios in winter (0.34 ± 0.13), and are almost constant in the other three
394 seasons. This trend is different from the one detected in the Central Himalayan region (1.07
395 in winter, 0.56 in summer) (Hegde and Kawamura, 2012) and Chennai, India (0.42 for winter,
396 0.29 for summer) (Pavuluri et al., 2010). In contrast, the values of Ph/C_9 are relatively high in
397 winter (1.40 ± 0.69) and summer (1.33 ± 0.39), followed by spring (0.92 ± 0.33) and autumn
398 (0.82 ± 0.39); its ratios are obviously lower than the values found in 14 other megacities in
399 China (2.71 for winter, 3.37 for summer) (Ho et al., 2007) but are a bit higher than those in
400 Tokyo (0.65 one year mean value) (Kawamura and Ikushima, 1993). From the outcomes
401 discussed above, we concluded the contribution from anthropogenic emissions as the main
402 source in megacities. Ph/C_6 ratios reached to the highest values in winter (4.06 ± 0.78) and the
403 lowest in autumn (1.66 ± 0.78). A previous study demonstrated that the Ph/C_6 ratio from
404 gasoline fuel vehicle (2.05) is lower than that from diesel fuel vehicles (6.58) (Kawamura and
405 Kaplan, 1987). In addition, most of the Ph/C_6 values are larger than unity during the whole
406 sampling year, which demonstrates that abundances of diacids attributable to more emissions
407 from diesel burning than gasoline fuel vehicles.

408 Maleic acid (M), originated predominantly from photochemical oxidation of aromatic
409 hydrocarbons (e.g., benzene and toluene), can be subsequently isomerized to its *trans*-isomer,
410 fumaric acid (F), under favorable conditions. Lower M/F values have been detected in
411 atmospheric aerosols over the North Pacific Ocean (0.3) (Kawamura and Sakaguchi, 1999) as
412 well as at Alert in the high Arctic (ratio range: 0.5–1.0) (Kawamura et al., 1996a). The M/F
413 ratios are almost constant in winter (2.0 ± 0.66) and spring (2.0 ± 0.67) and are higher than
414 those in autumn (1.67 ± 0.81) and summer (1.35 ± 0.49). This trend may be associated with
415 substantial amounts of precursors emitted from biomass burning in autumn, fresh aerosols
416 brought by high-speed wind in spring and enhanced isomerization reaction from M to F under
417 intense solar radiation in summer. The conversion of maleic to fumaric acids can be
418 restrained in polluted environments with minimum weak sunlight (Kundu et al., 2010a). Thus,



419 M may not be effectively isomerized to F during wintertime in Beijing. The high ratios of
420 M/F throughout the whole year imply that aerosols in Beijing are not seriously subjected to
421 secondary oxidation processes.

422 Based on field observations, Kawamura and Ikushima (1993) hypothesized that C₄ diacid can
423 transform into malic acid (hC₄) by means of hydroxylation. The hC₄/C₄ ratios were the
424 highest in warm seasons (0.04±0.01 in summer, 0.03±0.02 in spring), which supported this
425 hypothesis. hC₄/C₄ ratios in summer are 2–4 times larger than those in cold seasons, similar
426 to the trends observed in Jeju Island, Korea (Kundu et al., 2010b) and urban Tokyo
427 (Kawamura and Ikushima, 1993).

428 **3.4 Comparisons of the mean mass ratios between sampling sites**

429 To assess the emission strength of anthropogenic activities in Beijing, the mean values of (a)
430 C₃/C₄, (b) M/F, (c) Ph/C₉, (d) Ph/Tot and (e) tPh/Tot mass ratios were compared with those in
431 other sampling sites, including Xi'an (Wang et al., 2012), Gosan, Jeju Island (Kundu et al.,
432 2010a) and the western Pacific Ocean (Wang et al., 2006b). Xi'an, a megacity in the
433 Guanzhong Plain, is located in one of the regions heavily polluted by fossil fuel and biofuel
434 combustion. Atmospheric aerosols at the Gosan site are mixtures of westerly winds from high
435 latitude regions of Eurasia. Marine aerosols over the western Pacific Ocean are a combination
436 of long-range transported continental aerosols and locally emitted marine aerosols.

437 Figure 5 presents the global distribution of diagnostic mass ratios of diacids and related
438 compounds. Rather low C₃/C₄ ratios were observed in urban aerosols, including Beijing and
439 Xi'an, compared to those aged organic matters collected from Gosan and the western Pacific
440 Ocean. Similarly, larger C₃/C₄ ratios were obtained in summer than in the other seasons. The
441 same observation in Beijing may be attributable to the enhancement of secondary oxidation
442 that favors the conversion of C₄ diacid to C₃ diacid in the warm season; however, in that case,
443 the photochemical activity is insignificant compared to the primary emissions. Similar to the
444 C₃/C₄ ratios, low M/F ratios indicate the importance of photochemical reaction routes
445 (Kawamura and Sakaguchi, 1999). The mean values of M/F in the Beijing aerosols are larger
446 than or comparable to those reported in Gosan (spring: 1.38, summer: 0.76, autumn: 1.62, and



447 winter: 2.21) but lower than those obtained in Xi'an aerosols (summer: 2.22 and winter: 2.38),
448 indicating that the PM_{2.5} aerosols in Beijing are mainly linked with regional primary
449 emissions, whereas the photo-isomerization from *cis* to *trans* isomer is insignificant.

450 Usually, high Ph/C₉ ratios were detected in continental samples owing to a relatively strong
451 contribution from anthropogenic sources to dicarboxylic acids. A bit larger values of Ph/C₉
452 (in average) were obtained in Xi'an than those in Beijing because the air masses in Xi'an
453 were more heavily influenced by intense industrial emissions. Although the values of Ph/C₉
454 in both megacities were higher than those in the western Pacific Ocean, the wintertime Ph/C₉
455 ratios in Gosan were much greater than those in Beijing, which may be caused by the
456 secondary generation of abundant precursors, such as naphthalene, which were transported by
457 long-distance from East Asia.

458 In this study, we calculated the ratios (%) of Ph and tPh to total diacids, respectively, to
459 estimate the primary emission strength in different sampling sites. The largest mean mass
460 ratios of Ph/Tot were observed during winter in Beijing, while the values in the other seasons
461 were lower than those observed in Xi'an due to its basin-like topography. For the tPh/Tot
462 ratios, the mean values in Beijing were much higher than those in marine areas. However, the
463 average value of tPh/Tot in winter was lower than that in Xi'an. Thus, these comparisons
464 illustrate significant contributions from waste plastic burning and fossil fuel combustion in
465 Beijing during wintertime.

466 **3.5 Source identification by principal component analysis**

467 Previous studies have utilized principal component analysis (PCA) to discriminate the source
468 apportionment of atmospheric aerosols (Hopke, 1985). In this study, typical dicarboxylic
469 acids with other major components were chosen for factor analysis. Compounds with
470 common sources or photooxidation reactions would be likely to display similarities in mass
471 variations and be assorted into one "factor". High loadings of variables on the selected
472 species reveal closer links of sources and formation pathways between these compounds (Wu
473 et al., 2015). Here, "total varimax" maximizes the variance of the squared elements in the
474 columns of a factor matrix. The PCA result for dicarboxylic acids and other main



475 components in PM_{2.5} in Beijing from Sep. 2013 to Jul. 2014 is given in Table 4.

476 During the whole sampling period, the first factor accounted for 75.2% of the total variance
477 with high loadings of selected diacids, WSOC, and EC (a tracer for incomplete
478 combustion-generated carbon emissions). Typically, the prolonged photochemical oxidation
479 of organics in the atmosphere leads to enhanced concentrations of polar organic matters.
480 WSOC can account for 45–75% of aerosol carbon mass in biomass burning emissions
481 (Falkovich et al., 2005) and 20–60% of that in fossil fuel combustion-derived particles
482 (Pathak et al., 2011). Agricultural waste burning is a substantial pollution factor in Beijing
483 (Fig. 1) (Viana et al., 2008; Cheng et al., 2014), especially in late June and early October,
484 resulting in substantial organic aerosols (Fu et al., 2012). C₄, C₉, tPh, ωC₂, Pyr, Gly and
485 MeGly showed strong correlations in the first factor, implying that burning activities
486 contribute to a large fraction of their concentrations, including biomass burning, biofuel
487 combustion and burning of municipal wastes. For example, the photooxidation of *p*-xylene, a
488 main precursor of terephthalic acid dimethyl ester, can produce glyoxal (Simoneit et al., 2005;
489 Kawamura and Pavuluri, 2010).

490 EC, maleic and phthalic acids are well associated with other species, indicating that they
491 originate from common mixed sources that are mainly produced by anthropogenic emissions,
492 such as vehicular exhaust, fossil fuel combustion and biomass burning. Aromatic
493 hydrocarbons from incomplete combustions are key materials for maleic and phthalic acids
494 (Kawamura and Sakaguchi, 1999). Both M and Ph showed abundances under hazy conditions
495 (Mochida et al., 2003).

496 As for the second factor, Ph, tPh and EC weakly loaded with each other, which seems to
497 originate from motor emissions, fossil fuel combustion and waste plastic burning. WSOC
498 also showed a slight loading in the second factor, which indicates that anthropogenic
499 emissions also contribute to a certain amount of WSOC during the sampling periods.

500 3.6 Stable carbon isotopic compositions

501 The systematic differences in stable carbon isotope ratios of diacids and other polar acids
502 were attributable to kinetic isotope fractionation processes in the atmosphere (Hoefs and



503 Hoefs, 1997), while secondary oxidation of these water-soluble organic acids is more
504 influential for diacid carbons to enrich in ^{13}C (Wang and Kawamura, 2006c). For example,
505 the relatively short carbon-chain diacids enriched in ^{13}C were ascribed to the kinetic isotopic
506 effect (KIE) for the photochemical breakdown of longer-chain diacids (Anderson et al., 2004;
507 Irei et al., 2006). And lower dicarboxylic acids with enrichment of ^{13}C may be less active to
508 oxidants (e.g., OH radicals). Therefore, the determinations of $\delta^{13}\text{C}$ values of dicarboxylic
509 acids and related compounds show vital information about the atmospheric aging processes
510 of aerosols derived from local emissions or long-range transport ways in air.

511 Table 5 presents the stable carbon isotope ratios of major compounds. The mean $\delta^{13}\text{C}$ values
512 of C_2 , C_3 and C_9 were constant among seasons, but those of C_4 , ωC_2 , Pyr were smaller in
513 summer than in winter. Because coal is more enriched in ^{13}C than that of petroleum fuel
514 (Court et al., 1981; Kawashima and Haneishi, 2012), the ^{13}C enrichment of these organic
515 acids during wintertime may be attributable to the enhanced coal incineration for house
516 heating. Mean $\delta^{13}\text{C}$ values of malonic acid in autumn and spring were similar to those of
517 succinic acid, suggesting that they may have similar sources or the same secondary formation
518 pathways.

519 The mean seasonal $\delta^{13}\text{C}$ values of C_9 varying from -25.6‰ to -26.9‰ were smaller than
520 those of C_2 – C_4 diacids. This signature demonstrates unsaturated fatty acids derived from
521 terrestrial vegetation as one key source of C_9 , because more depletion of ^{13}C in continental
522 higher plants in comparison with the particulate organic matters from marine plankton
523 activities. The $\delta^{13}\text{C}$ values of C_9 suggested that azelaic acid is mainly from anthropogenic
524 primary emissions, especially biomass burning in the surrounding areas.

525 As mentioned earlier, Ph is mainly formed via the photochemical processes of polycyclic
526 aromatic hydrocarbons, but it can be emitted directly from fossil fuel combustion as well
527 (Kawamura and Kaplan, 1987; Fraser et al., 2003). The largest $\delta^{13}\text{C}$ value of Ph in winter was
528 linked with its peak concentrations. This finding may be ascribed to the intensity of coal and
529 gasoline combustion in Beijing, especially the stagnant atmospheric conditions in favor of
530 accumulation of organic matters during wintertime (Cao et al., 2011). In general, the organic
531 aerosols derived from coal and gasoline burnings are more enriched in ^{13}C than other



532 emissions, including diesel combustion, aerosols released from C₃-plants, and secondary
533 organic matters.

534 For terephthalic acid, the lowest $\delta^{13}\text{C}$ value of tPh (ave: -33.5‰) in winter supports the
535 finding that it is directly emitted from the burning of plastic wastes. Waste burning usually
536 contains many plastics and occurs frequently in open spaces without emission control
537 (Kawamura and Pavuluri, 2010), in addition to other local anthropogenic emissions. Lighter
538 $\delta^{13}\text{C}$ values of major compounds in Beijing than those in the marine and Arctic areas may be
539 explained by more contributions of primary emissions from anthropogenic sources.

540 Box plots of stable carbon isotope ratios ($\delta^{13}\text{C}$ values) are displayed in Fig. 6 for seasonal
541 distributions of diacids, glyoxylic and pyruvic acids in PM_{2.5}. There is a decreasing trend in
542 $\delta^{13}\text{C}$ for C₅ to C₉. Succinic acid showed the heaviest $\delta^{13}\text{C}$ value (-17.1‰) among all species
543 in winter and spring, while malonic acid was more enriched in ^{13}C than others in autumn ($-$
544 17.6‰) and summer (-18.7‰). Such trends were not observed for C₃ and C₄ diacids. A
545 previous study noted that increasing concentrations of oxalic and malonic acids inhibit the
546 growth of total fungi number due to the lower pH, which in turn changes the efficiency of
547 fungi to degrade the malonic acid (Côté et al., 2008). Hence, an enrichment of ^{13}C in
548 remaining malonic acid may be interpreted by the isotopic fractionations occurring in the
549 breakdown ways of dicarboxylic acids or photochemical degradation of C₃ diacid. In this
550 study, the median $\delta^{13}\text{C}$ values of ωC_2 were much lower than those of C₂ in all seasons,
551 whereas $\delta^{13}\text{C}$ of Pyr showed median values similar to C₂ in autumn and spring, which are
552 surprisingly higher than that of C₂ in autumn.

553 3.7 Relations between $\delta^{13}\text{C}$ values and air mass source areas

554 In order to further estimate the impacts of air mass source regions on $\delta^{13}\text{C}$ values of specific
555 compounds, five-day backward trajectories for each aerosol sample are illustrated in Figure 1.
556 Data from urban Sapporo (Aggarwal and Kawamura, 2008), Gosan of the Jeju Island (Zhang
557 et al., 2016) and remote marine regions (Wang and Kawamura, 2006c) are plotted together
558 with the seasonal mean $\delta^{13}\text{C}$ values of major species detected in this study (Fig. 7). The
559 largest average $\delta^{13}\text{C}$ value of oxalic acid was observed in the Gosan samples. The seasonal



560 mean $\delta^{13}\text{C}$ values of malonic acid in Beijing were higher than those in Sapporo and remote
561 marine areas, but C_3 was less enriched in ^{13}C compared to Gosan owing to the degradation of
562 C_3 diacid or C_2 diacid depleted in ^{13}C . The mean $\delta^{13}\text{C}$ values of succinic acid are comparable
563 to those in the other three places, except during summer. The mean $\delta^{13}\text{C}$ values of Pyr in
564 autumn (-19.6‰) and spring (-22.3‰) were similar to the data in Sapporo (-20.3‰) and
565 Gosan (autumn: -19‰ , winter: -22.2‰ , spring: -19.1‰ , summer: -17.6‰) aerosols. The
566 $\delta^{13}\text{C}$ values of ωC_2 and Ph in remote marine samples are the highest, followed by those for
567 Sapporo and Gosan sites and then Beijing. In contrast, the seasonal mean $\delta^{13}\text{C}$ values of C_6
568 and C_9 in Beijing are similar to those in Sapporo and Gosan aerosols but lower than those in
569 marine aerosols.

570 The air masses in Gosan, Jeju Island and Sapporo are mixtures of the flows from the
571 mainland of East Asia. The $\delta^{13}\text{C}$ values illustrate that organic aerosols in Sapporo are formed
572 via photooxidation of precursors originated from anthropogenic and biogenic emissions (e.g.,
573 biomass burning) to a large extent, especially for C_6 and C_9 ; however, the study in Gosan
574 found that aerosol samples are more aged in the western North Pacific rim. Most importantly,
575 particulate organic matters in remote marine areas are intensively aged during long-range
576 transport and are affected by both the sea-to-air emissions and the terrestrial outflows.
577 Moreover, the enrichment in ^{13}C can be regarded as a result of the isotopic fractionation for
578 aged aerosols. Urban aerosols from Beijing, where the air masses are mixed with those
579 originating from Siberia and surrounding areas, are seriously affected by biomass/biofuel
580 burning in the whole year. Compared with the $\delta^{13}\text{C}$ values in Gosan, Sapporo and remote
581 marine areas, the smaller $\delta^{13}\text{C}$ values of organic compounds in Beijing may be caused by the
582 different emission strengths of various primary sources.

583 **3.8 Relations between $\delta^{13}\text{C}$ values and photochemical aging**

584 C_2/Tot ratio is suggested to be a useful tracer to evaluate the aging of atmospheric aerosols
585 (Kawamura and Sakaguchi, 1999). The mean $\delta^{13}\text{C}$ values of oxalic acid showed the smallest
586 value in winter (-22.9‰) and showed the highest value in autumn (-20.1‰), followed by
587 spring (-21.9‰) (Fig. 8a). Here, we compared the $\delta^{13}\text{C}$ values of C_2 and its concentration



588 changes with the relative abundance of C₂ to total diacids (Fig. 8b). The isotopic ratio values
589 of C₂ were positively correlated with C₂/Tot ratios in autumn ($r^2=0.45$) and winter ($r^2=0.29$),
590 suggesting that production of C₂ from the oxidation of precursors can contribute to the
591 increase of $\delta^{13}\text{C}$ values (Pavuluri et al., 2011). Due to enhanced primary emissions from coal
592 combustion and biomass burning, stagnant atmospheric inversion can favor the accumulation
593 of pollutants. Furthermore, the $\delta^{13}\text{C}$ values of tPh decreased from autumn to winter, followed
594 by an increase toward summer (Fig. 9). Seasonal $\delta^{13}\text{C}$ values of tPh decreased with the
595 enhanced ratios of tPh to total diacids (tPh/Tot) in autumn ($r^2 = 0.35$) and winter ($r^2 = 0.19$),
596 indicating large emissions from municipal waste burning activities in cold seasons, especially
597 in winter.

598 Aged organic aerosols are characterized by high abundance of polar and water-soluble
599 organic species, leading to high values of WSOC/OC ratio. However, in the Beijing samples,
600 the $\delta^{13}\text{C}$ values of major species (C₂, C₃, C₄, C₉, ωC_2 , Pyr, Ph and tPh) did not show strong
601 relationships with the WSOC/OC ratios in this paper (Fig. 10). The $\delta^{13}\text{C}$ values of C₃ only
602 correlated well with the WSOC/OC ratios in summer ($r^2 = 0.57$), in conformity with the
603 variation of C₃/C₄ ratios, which illustrates an enhanced degree of photochemical processing
604 of diacids during summertime. The $\delta^{13}\text{C}$ values of C₄ were negatively correlated with
605 WSOC/OC ratios in the cold seasons (autumn: 0.31, winter: 0.45), demonstrating an
606 enrichment of $\delta^{13}\text{C}$ in C₄ with decreasing WSOC/OC ratios. Ph displayed negatively weak
607 correlations in summer, while ωC_2 presented weakly positive and negative relations in
608 autumn (0.2) and spring (0.29), respectively. The positive relationship between the $\delta^{13}\text{C}$
609 values of Pyr and WSOC/OC in autumn (0.62) suggests that an isotopic enrichment of Pyr
610 increases with high WSOC/OC ratios, which may have resulted in the largest $\delta^{13}\text{C}$ values of
611 Pyr in autumn. There are no correlations between C₂, tPh and C₉ with the WSOC/OC ratios in
612 the Beijing samples. Thus, the results discussed above suggest that primary emissions in local
613 regions significantly impact diacids and related compounds in Beijing.

614



615 **4 Summary and conclusions**

616 In this study, the molecular distribution and stable carbon isotopic composition of diacids,
617 oxoacids, and α -dicarbonyls were determined in fine aerosol samples ($PM_{2.5}$) in Beijing over
618 one year. Oxalic acid was found to be the most abundant diacid throughout the year. The
619 concentration patterns of major identified organic compounds varied among different seasons.
620 Such differences in molecular compositions were caused by diverse emission strengths of
621 primary emission sources together with photooxidation processes in Beijing. Correlation
622 analyses of main oxoacids and α -dicarbonyls with combustion tracers (Cl^- and K^+) indicate
623 that ωC_2 , Pyr, Gly and MeGly were mostly affected by biogenic combustions in whole
624 sampling year, with significant contribution of fossil fuel combustion in winter. The
625 variations in the C_3/C_4 ratios were relatively minor during the one-year observation, with
626 most values less than or equal to unity, which is associated with the substantial emissions
627 from vehicular exhausts. Higher ratios of Ph/Tot and tPh/Tot were observed in winter,
628 indicating strong influences of fossil fuel combustion and burning of plastic waste.

629 Larger $\delta^{13}C$ values obtained in lower carbon-numbered diacids are mainly interpreted as
630 isotopic fractionations due to the decomposition of longer-chain dicarboxylic acids and
631 related precursors. Although oxalic acid has been regarded as a final product of the
632 photooxidation of homologues diacids and related components like Pyr, ωC_2 and
633 α -dicarbonyls in the atmosphere, succinic acid showed the largest $\delta^{13}C$ value (-17.1%)
634 among all the species in winter and spring, while malonic acid was more enriched in ^{13}C than
635 others in autumn (-17.6%) and summer (-18.7%). The less negative $\delta^{13}C$ value of malonic
636 acid may be interpreted by the isotopic fractionations occurring in the breakdown of diacids
637 or photochemical degradation of C_3 diacid.

638 On the basis of the weak correlations of C_2/Tot and WSOC/OC with seasonal $\delta^{13}C$ values of
639 major species, the results of the principal component analysis, and the comparison of $\delta^{13}C$
640 values in Beijing with those in urban and remote marine aerosols, we can conclude that
641 photochemical production of dicarboxylic acids and related compounds in the Beijing
642 aerosols was insignificant in the whole sampling period. The abundance of diacids and



643 related polar acids in fine aerosols in Beijing are mainly associated with anthropogenic
644 primary emissions such as biomass burning, fossil fuel combustion and plastic burning.
645 Further study is needed to interpret the detailed mechanisms of the enrichment of the $\delta^{13}\text{C}$
646 values of C_3 and C_4 diacids and to better evaluate the impact of micro-biological degradation
647 along with contact-induced chemical changes on the aerosol chemistry in Beijing.

648

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937 **Table 1.** Seasonal concentrations (ng m^{-3}) of dicarboxylic acids, ketocarboxylic acids and
 938 α -dicarbonyls in $\text{PM}_{2.5}$ samples collected in Beijing from 30 September 2013 to 12 July 2014.

Species (Abbr.)	Autumn (n=16)		Winter (n=15)		Spring (n=19)		Summer (n=15)	
	Range	Mean/SD	Range	Mean/SD	Range	Mean/SD	Range	Mean/SD
Dicarboxylic acids								
Oxalic, C ₂	31–1760	472/490	44.9–456	149/123	96.5–496	262/120	64.7–462	267/146
Malonic, C ₃	6.0–132	43.5/36.1	5.8–54.2	20.1/15.6	8.4–64.9	33.0/14.2	13.9–46.9	30.5/13.0
Succinic, C ₄	11.5–231	67.2/62.1	11.1–81.0	31.6/21.3	11.4–82.0	37.7/17.4	14.5–54.8	31.2/14.0
Glutaric, C ₅	2.8–50.3	15.2/13.6	3.5–20.9	9.2/5.6	4.9–17.8	10.3/3.8	4.4–13.9	8.8/3.4
Adipic, C ₆	4.4–38.8	16.2/9.0	2.9–19.0	8.9/5.0	5.9–21.1	13.6/3.8	4.9–16.7	10.6/4.0
Pimelic, C ₇	0.8–16.7	6.0/6.4	0.6–11.4	3.4/3.4	1.7–7.4	3.9/1.8	1.1–5.2	3.0/1.2
Suberic, C ₈	BDL–24.3	4.7/7.3	BDL	BDL	BDL–10	2.3/3.3	BDL–5.1	0.8/1.6
Azelaic, C ₉	13.7–59.3	31.6/14.2	12.1–60.3	27.3/14.7	15.1–60	27.2/11.1	11.0–28.2	19.0/5.0
Decanedioic, C ₁₀	0.2–7.7	2.3/2.0	0.4–2.6	1.2/0.6	0.7–3.2	1.6/0.8	0.9–3.0	1.7/0.6
Undecanedioic, C ₁₁	0.4–10.0	2.7/2.4	0.6–5.7	2.2/1.6	1.1–3.1	2.0/0.6	1.1–2.4	1.8/0.5
Dodecanedioic, C ₁₂	BDL–2.1	0.5/0.5	BDL–1.8	0.1/0.5	BDL–0.5	0.2/0.2	BDL–0.5	0.2/0.2
Methylmalonic, iC ₄	0.1–3.3	1.1/0.8	0.3–2.3	1.0/0.6	0.5–3.0	1.1/0.6	0.5–1.9	0.9/0.4
Methylsuccinic, iC ₅	1.3–24.7	7.3/6.8	2.2–14.5	5.7/3.8	1.4–6.8	3.8/1.9	0.7–3.8	2.2/0.9
2-methylglutaric, iC ₆	0.2–6.6	1.8/1.8	0.3–2.9	1.1/0.7	0.4–1.8	1.0/0.5	0.3–1.3	0.8/0.4
Maleic, M	1.0–12.6	3.7/3.1	1.2–6.6	3.0/1.6	1.1–6.3	2.5/1.4	1.0–3.3	1.8/0.7
Fumaric, F	0.4–11.3	3.0/3.0	0.4–4.5	1.8/1.5	0.5–3.0	1.4/0.8	0.7–2.6	1.5/0.7
Methylmaleic, mM	1.1–17.3	5.2/4.7	1.7–11.7	4.8/3.1	1.3–5.8	2.5/1.6	0.8–4.6	2.2/1.1
Phthalic, Ph	7.6–58.7	25.5/15.8	11.4–98.5	37.9/27.2	8.5–36.7	22.5/7.1	13.4–42.3	24.9/8.0
Isophthalic, iPh	0.5–6.2	1.9/1.6	0.5–4.2	1.8/1.2	BDL–2.6	0.7/0.6	0.3–1.1	0.8/0.3
Terephthalic, tPh	8.9–80.4	40.3/25.0	10.8–136	48.7/41.1	4.6–35.3	19.5/9.3	5.2–26.0	15.5/6.0
Malic, hC ₄	BDL–6.5	1.3/2.0	BDL–0.8	0.2/0.3	0.4–4.5	1.2/1.3	0.5–4.0	1.2/1.0
Oxomalonic, kC ₃	0.7–24.2	6.8/6.7	1.3–18.0	5.0/4.7	0.8–12.7	6.5/3.5	1.1–8.7	4.2/2.4
4-oxopimelic, kC ₇	0.3–8.8	3.0/2.5	0.3–5.8	1.6/2.1	0.8–7.2	3.2/1.7	1.3–10.2	4.7/2.9
Total diacids	110–2580	763/701	113–1010	366/261	158–781	460/180	171–722	435/195
Oxocarboxylic acids								
Pyruvic, Pyr	2.0–56.0	15.6/14.9	2.6–68.7	13.5/17.6	4.5–21.7	11.5/5.3	3.6–19.3	10.9/6.0
Glyoxylic, ω C ₂	3.3–183	43.7/50.4	6.9–275	44.3/69.0	7.3–61.1	25.1/15.3	4.0–49.7	24.7/17.0
3-oxopropanoic, ω C ₃	0.6–23.5	6.0/6.2	0.8–23.1	5.6/6.2	1.0–8.2	4.7/2.2	1.4–7.2	3.7/1.7
4-oxobutanoic, ω C ₄	2.1–41.3	11.9/10.6	2.9–32.2	10.5/9.0	3.0–14.2	8.0/3.5	1.9–12.1	6.5/3.3
5-oxopentanoic, ω C ₅	0.7–8.2	2.7/2.1	0.8–6.7	2.5/1.7	0.8–4.1	2.2/0.9	0.7–3.5	1.8/0.9
7-oxoheptanoic, ω C ₇	0.5–7.0	3.0/2.0	0.4–5.0	1.9/1.6	1.0–4.8	3.1/1.0	1.6–6.9	3.5/1.5
8-oxooctanoic, ω C ₈	0.4–12.3	4.0/3.3	0.2–9.2	2.4/2.7	0.4–6.6	3.0/1.4	2.4–9.2	5.2/2.4
9-oxononanoic, ω C ₉	0.4–7.2	2.0/1.8	0.6–2.9	1.6/0.8	0.3–1.9	1.1/0.4	0.2–2.2	1.1/0.6
Total ketoacids	9.5–282	73.3/76.3	13.5–353	68.7/91.0	14.5–95.0	47.3/24.6	15.1–82.8	46.5/27.0
α-dicarbonyls								
Glyoxal, Gly	0.6–36.6	9.3/10.8	1.5–31.0	7.2/8.1	1.8–9.8	4.2/2.3	0.9–7.9	3.8/2.5
Methylglyoxal, MeGly	1.0–49.3	15.9/17.3	1.5–30.9	8.3/7.9	1.5–26.1	8.5/6.8	1.7–22.3	9.0/7.2
Total dicarbonyls	1.5–85.9	25.1/28.1	3.7–61.9	15.5/15.9	3.9–35.9	12.7/9.1	2.6–30.1	12.7/10.0

939 BDL: below detection limit, which is ca. 0.005 ng m^{-3} for the target compounds.

940



941 **Table 2.** Comparison of characteristics of diacids at the Beijing site and its other areas detected from previous studies.

Location	Sampling Date	Size	Diacid (C ₂ -C ₁₂) Concentrations (Mean) ng m ⁻³	Major Species	Diacid-C/OC (Diacid-C/TC) %	WSOC/OC (WSOC/TC) %	Reference
Fourteen Chinese cities	Jun-Jul 2003	PM _{2.5}	211–2162 (892)	C ₂ >Ph>C ₄ >C ₃	2.3 (1.4 ^b)	48 (37)	Ho et al. [2007]
Fourteen Chinese cities	Jan 2003	PM _{2.5}	319–1940 (904)	C ₂ >C ₄ >Ph>C ₃	1.3 (1.0 ^b)	41 (32)	Ho et al. [2007]
Xi'an, China	Jan-Feb 2009	PM ₁₀	1033–2653 (1843)	C ₂ >Ph>Ph>Ph>ωC ₂	1.1 ^b (0.83)	54 ^b (41 ^b)	Cheng et al. [2013]
Xi'an, China	Aug 2009	PM ₁₀	478–2040 (1259)	C ₂ >Ph>C ₄ >C ₃	4.4 ^b (3.8 ^b)	80 ^b (52 ^b)	Cheng et al. [2013]
Beijing, China	Sep-Oct 2007	TSP	105–3056 (1208)	C ₂ >C ₄ >C ₃ >Ph	(3.0)		He et al. [2014]
Hong Kong, China	Aug 2003	PM _{2.5}	260–677 (454)	C ₃ >Ph>Ph>Ph>Ph	0.41		Wang et al. [2006a]
Hong Kong, China	Feb 2004	PM _{2.5}	114–812 (771)	C ₂ >Ph>Ph>Ph>Ph	0.51		Wang et al. [2006a]
Sapporo, Japan	May-Jul 2005	TSP	106–787 (406)	C ₂ >C ₃ >C ₄ >Ph	4.8 (1.8)	44 (39)	Aggarwal and Kawamura [2008]
Chennai, India	Jan-Feb, May 2007	PM ₁₀	176–1436 (612)	C ₂ >C ₃ >C ₄ >Ph	(1.6)		Pavuluri et al. [2010]
Gosan, South Korea	Apr 2003-Apr 2004	TSP	142–1875 (636)	C ₂ >C ₃ >C ₄ >ωC ₂	(0.95)		Kundu et al. [2010b]
Tokyo, Japan	Apr 1988-Feb 1989	TSP	90–1360 (480)	C ₂ >C ₃ >C ₄ >C ₉	(0.95)		Kawamura and Ikushima [1993]
Ulaanbaatar, Mongolia	Nov 2007-Jan 2008	PM _{2.5}	146–779 (536)	Ph>C ₂ >C ₄ >Ph	0.8 (0.6)	53.2 (43.8)	Jung et al. [2010]
Chengdu, China	Jan 2013 (Daytime)	PM _{2.5}	1490–4690 (3450)	C ₂ >C ₄ >Ph>Ph	2.3 ^b (4.8 ^b)		Li et al. [2015]
Chengdu, China	Jan 2013 (Nighttime)	PM _{2.5}	1410–5250 (3330)	C ₂ >C ₄ >Ph>Ph	2.2 ^b (4.2 ^b)		Li et al. [2015]
Beijing, China	Sep 2013-Jul 2014	PM _{2.5}	110–2580 (506)	C ₂ >C ₃ >ωC ₂ >C ₃	2.0 ^b (1.5 ^b)	60 ^b (45 ^b)	This study

^b Calculated from the mean values from the references.

944 **Table 3.** Average seasonal variations in the ratios of diacids and related compounds.

Ratios	Autumn	Winter	Spring	Summer
C ₂ /Total diacids (%)	0.54±0.12	0.39±0.05	0.56±0.07	0.58±0.1
C ₃ /C ₄ ratio	0.69±0.14	0.59±0.11	0.88±0.09	0.99±0.1
C ₆ /C ₉ ratio	0.53±0.24	0.34±0.13	0.55±0.21	0.59±0.28
Ph/C ₉ ratio	0.82±0.39	1.4±0.69	0.92±0.33	1.33±0.39
Ph/C ₆ ratio	1.7±0.78	4.1±0.78	1.8±0.85	2.5±0.76
M/F ratio	1.7±0.81	2.0±0.66	2.0±0.67	1.4±0.49
hC ₄ /C ₄ ratio	0.01±0.01	0.01±0.01	0.03±0.02	0.04±0.01
C ₉ /Total diacids (%)	0.07±0.06	0.09±0.03	0.07±0.03	0.05±0.02
Ph/Total diacids (%)	0.04±0.02	0.11±0.01	0.05±0.02	0.07±0.03
C ₆ /Total diacids (%)	0.03±0.02	0.03	0.03±0.01	0.03±0.02
WSOC/OC ratio	0.70±0.27	0.49±0.11	0.56±0.07	0.58±0.10

945



946 **Table 4.** Results of the principal component analyses for selected diacids and related
947 compounds in PM_{2.5} in Beijing.

Species	Whole year	
	Factor 1	Factor 2
C ₂	0.87	
C ₃	0.89	
C ₄	0.92	
C ₆	0.74	
C ₉	0.72	
M	0.94	
F	0.96	
Ph	0.76	0.51
tPh	0.78	0.55
ωC ₂	0.92	
Pyr	0.92	
Gly	0.97	
MeGly	0.88	
WSOC	0.89	0.38
EC	0.81	0.46
Total variance	75.2%	10.9%

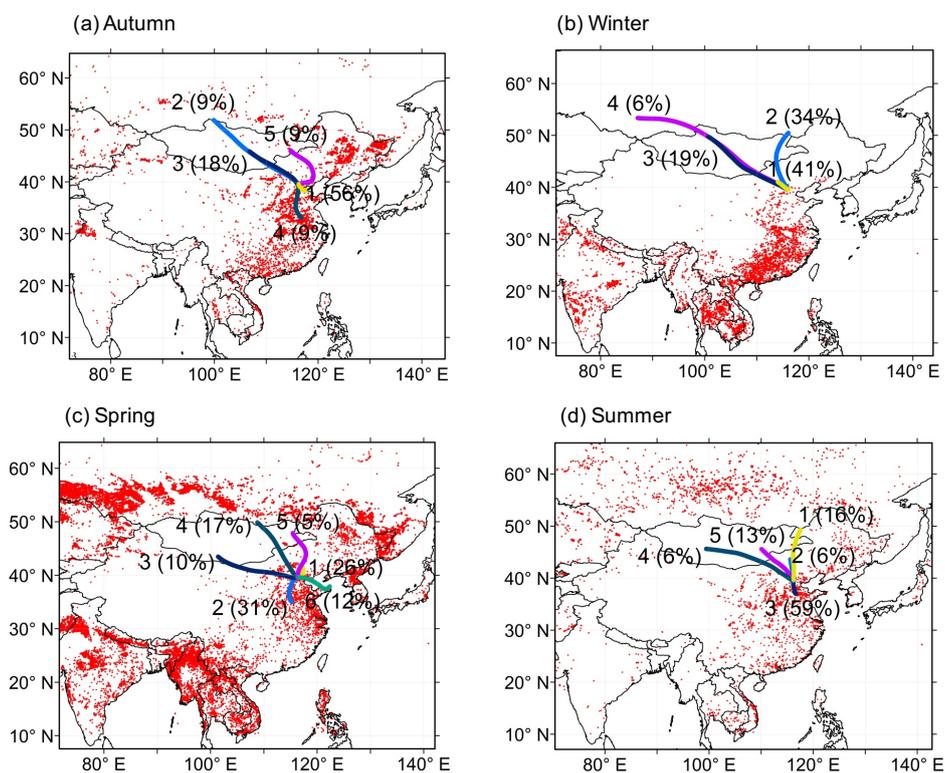
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949



950 **Table 5.** Stable carbon isotope ratios ($\delta^{13}\text{C}$, ‰) of major compounds in $\text{PM}_{2.5}$ in Beijing.

Species	Autumn			Winter			Spring			Summer		
	Min	Max	Mean±SD									
C ₂	-23.7	-15	-20.1±3.0	-27.2	-14.8	-22.9±3.4	-25	-16.6	-21.9±2.1	-27	-19.1	-22.4±2.7
C ₃	-27.2	-12.3	-17.6±4.6				-25.2	-5.6	-17.3±8.6	-24	-12.6	-18.7±4
C ₄	-25.2	-15.8	-19.8±2.3	-22.1	-9.8	-17.1±3.9	-20.6	-13.1	-17.1±2.0	-37.6	-19.4	-28.6±6.8
C ₅	-22.9	-31.8	-25.9±2.6	-29.7	-26.3	-28±1.5	-28.4	-23.5	-25.4±1.9			
C ₆	-43.2	-22.4	-28.5±8.5				-28.1	-24.5	-26.1±1.6			
C ₉	-31.3	-21.4	-26.4±2.6	-28.2	-23.7	-25.6±1.4	-31.3	-23.1	-26.9±2.0	-28.6	-20.8	-25.9±2.4
ωC ₂	-47.1	-26.3	-37.2±7.3	-61.6	-19.6	-32±13.7	-44	-19.4	-32.5±7.6	-44.3	-18.8	-32.2±7.3
Pyr	-29.1	-14.8	-19.6±5.9	-32.8	-16.7	-27.3±9.2	-38.1	-12.6	-22.3±9.7	-62.4	-19.0	-38.1±16
Ph	-47.5	-25.3	-32.6±7.9	-30.7	-25.1	-27.7±1.5	-33	-25.1	-28.3±1.9	-32.5	-27.6	-30.4±1.3
tPh	-27.6	-23.6	-25.2±1.0	-40.1	-28.5	-33.5±3.4	-33.4	-22.8	-25.8±3	-26.1	-18.9	-23.5±2.3

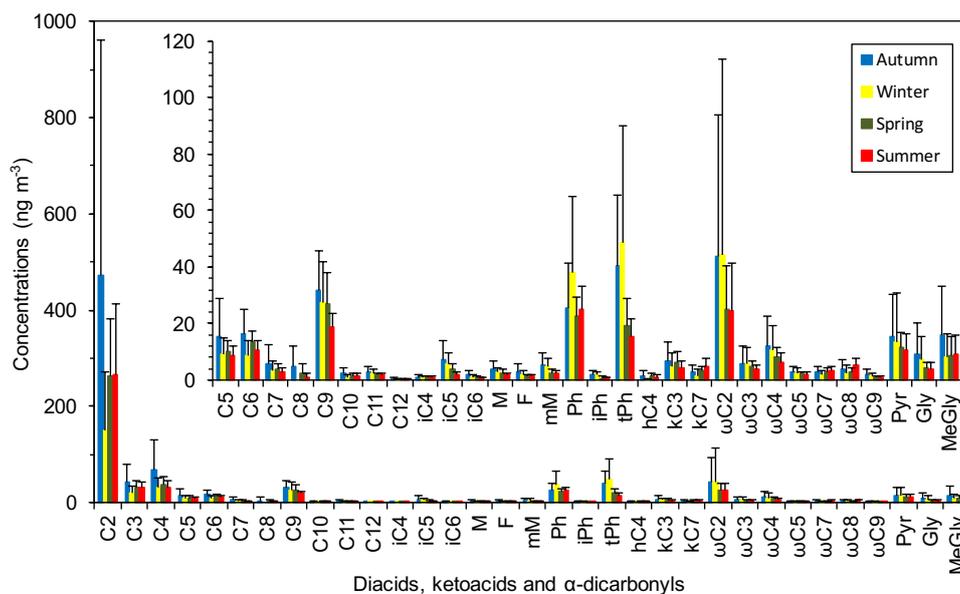


953

954

955 **Figure 1.** Fire spots with typical five-day air mass backward trajectories (mean clusters)
956 arriving at Beijing for each sampling season. The fire spot data were obtained from the MODIS
957 fire spot website (<https://firms.modaps.eosdis.nasa.gov/download/request.php>). The air mass
958 trajectories were drawn using the data obtained by HYSPLIT4 model from the NOAA ARL
959 website (<http://ready.arl.noaa.gov/HYSPLIT.php>). The arrival height of the air mass backward
960 trajectories was 500 m above sea level.

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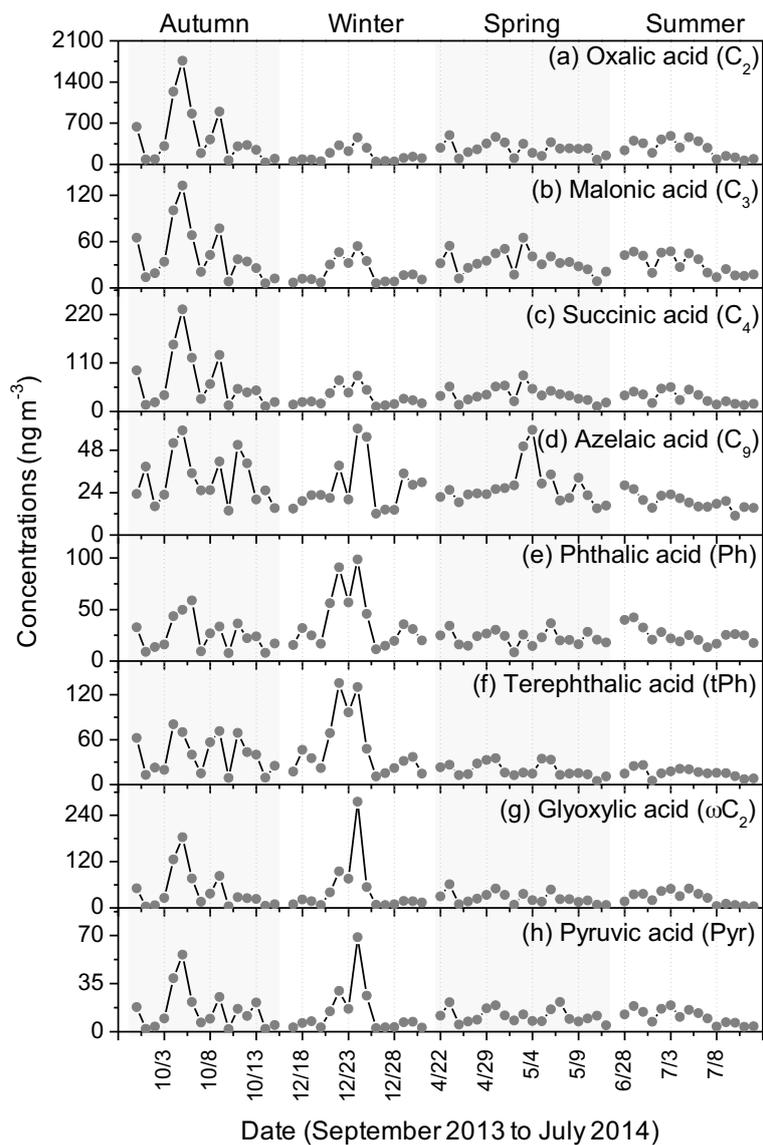


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963

964 **Figure 2.** Molecular distributions of dicarboxylic acids and related compounds in the PM_{2.5}
965 samples collected in Beijing from 30 September 2013 to 12 July 2014.

966

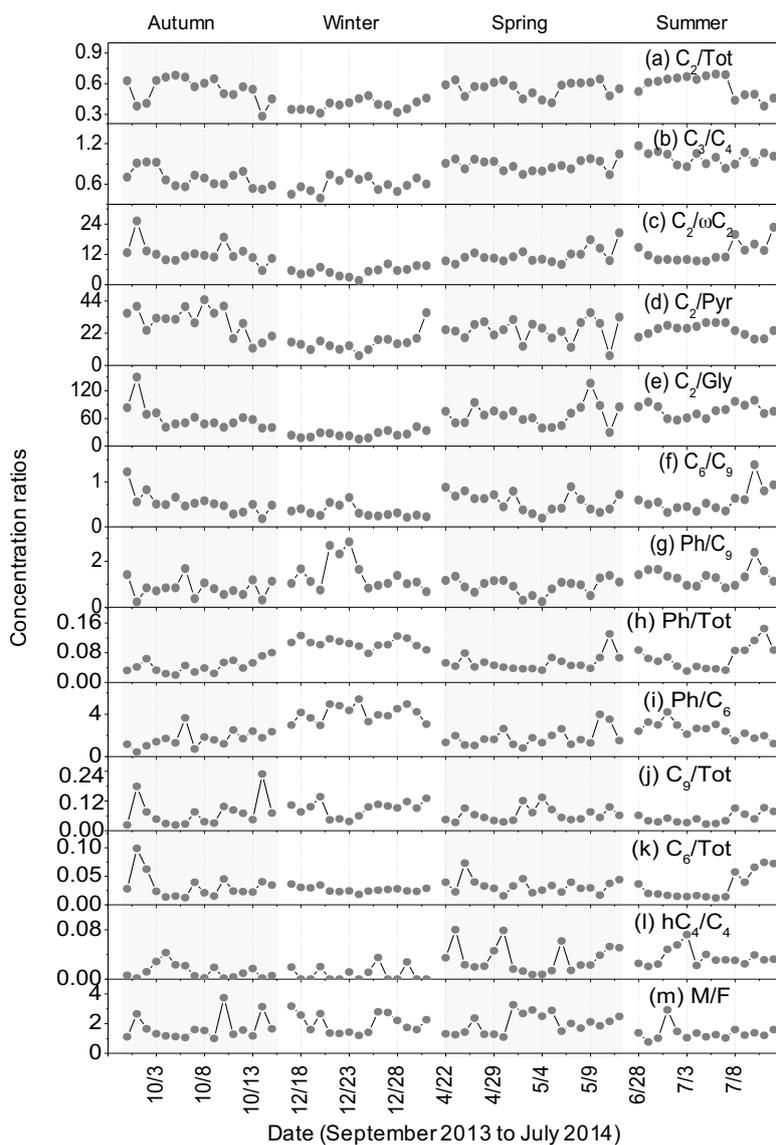


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969 **Figure 3.** Daily variations in the concentrations of selected organic acids in the PM_{2.5} aerosols
970 in Beijing.

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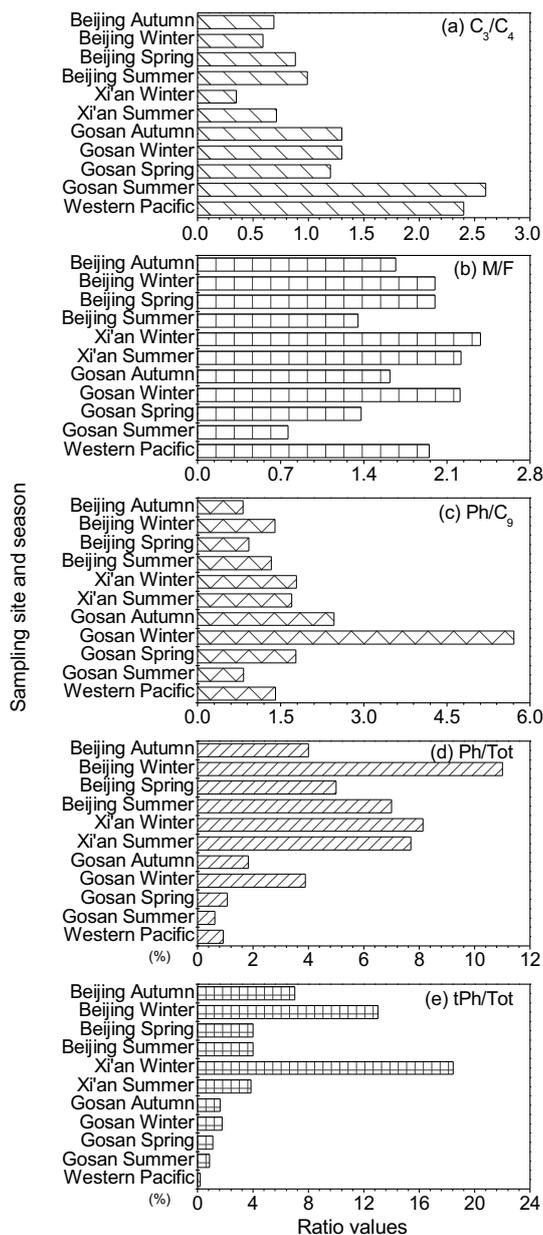


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974 **Figure 4.** Seasonal variations in the concentration ratios of (a) C_2/Tot , (b) C_3/C_4 , (c) $C_2/\omega C_2$,
 975 (d) C_2/Pyr , (e) C_2/Gly , (f) C_6/C_9 , (g) Ph/C_9 , (h) Ph/Tot , (i) Ph/C_6 , (j) C_9/Tot , (k) C_6/Tot , (l)
 976 hC_4/C_4 , and (m) M/F in the Beijing aerosols.

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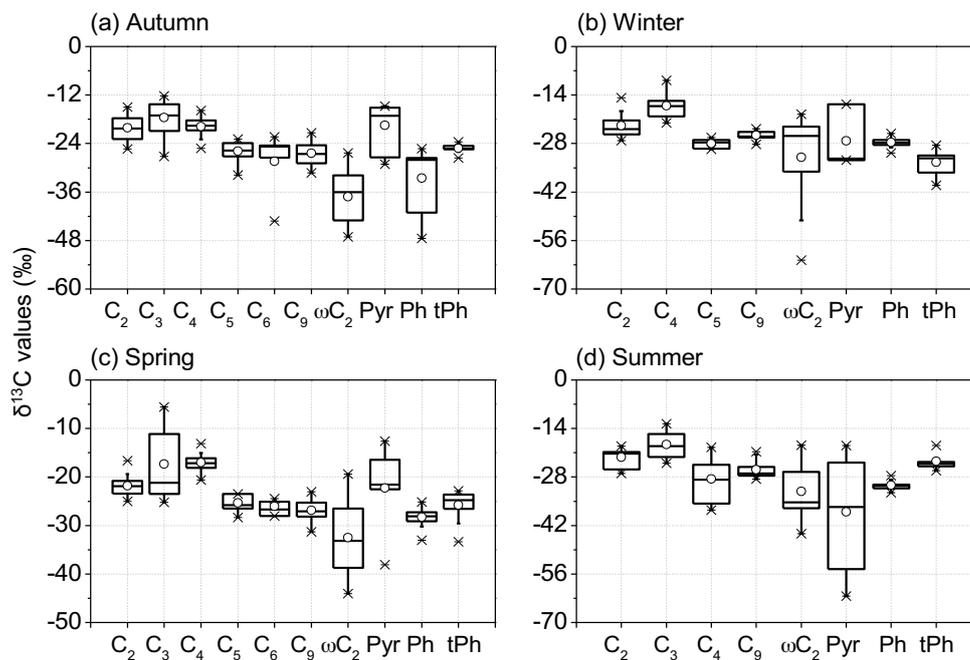


978

979

980 **Figure 5.** Mean mass ratios of (a) C_3/C_4 , (b) M/F, (c) Ph/ C_9 , (d) Ph/Tot, and (e) tPh/Tot from
981 this study compared with those in Xi'an (Wang et al., 2012), Gosan, Jeju Island (Kundu et al.,
982 2010a) and the western Pacific (Wang et al., 2006b) aerosols.

983



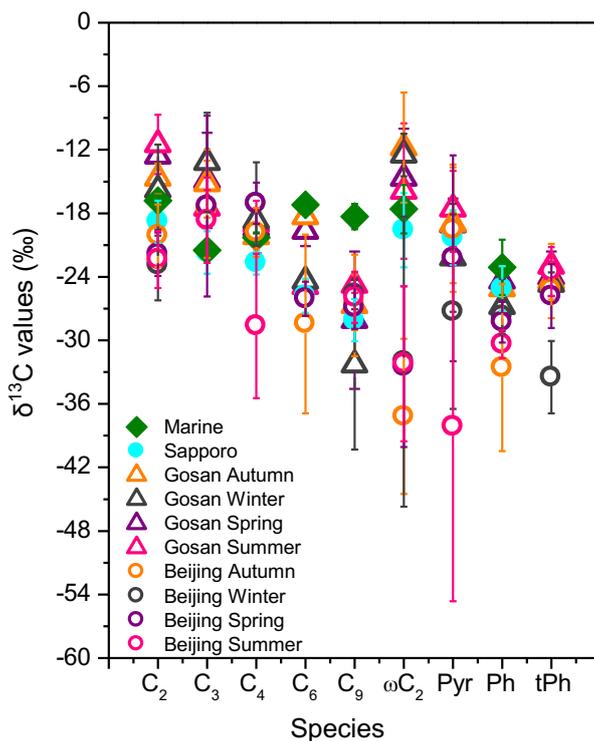
Diacids, glyoxylic and pyruvic acids

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985

986 **Figure 6.** Box plot of the $\delta^{13}\text{C}$ values of diacids, glyoxylic and pyruvic acids. The small circles
987 represent the average $\delta^{13}\text{C}$ values.

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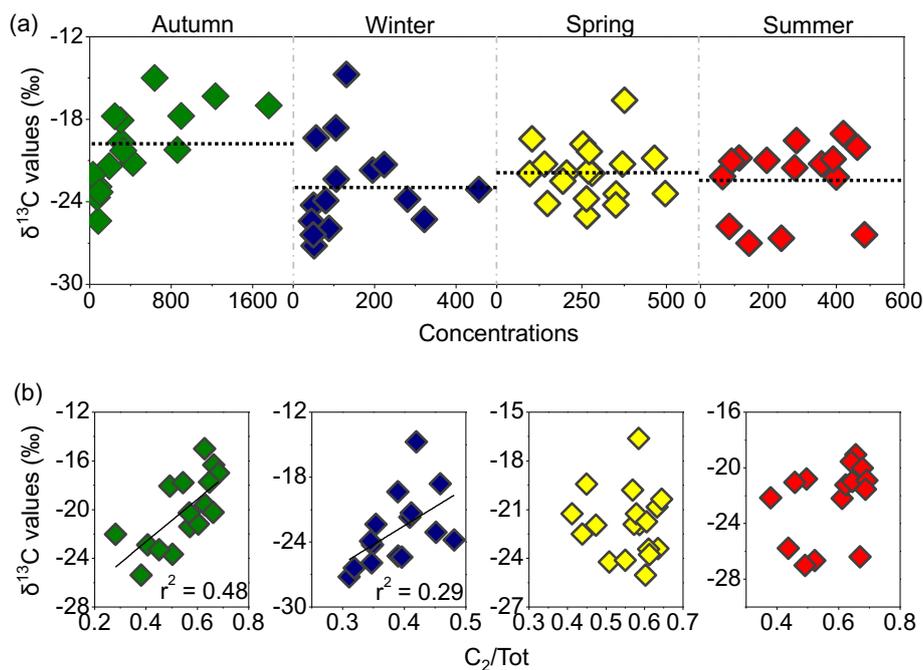


989

990

991 **Figure 7.** Seasonal mean $\delta^{13}\text{C}$ values of selected diacids and related compounds detected in
 992 PM_{2.5} in Beijing. Data from Sapporo (Aggarwal and Kawamura, 2008), Gosan, Jeju Island
 993 (Zhang et al., 2016) and marine (Wang and Kawamura, 2006c) aerosols are also plotted. The
 994 bar represents the standard variation ($\pm\text{SD}$) in the $\delta^{13}\text{C}$ values.

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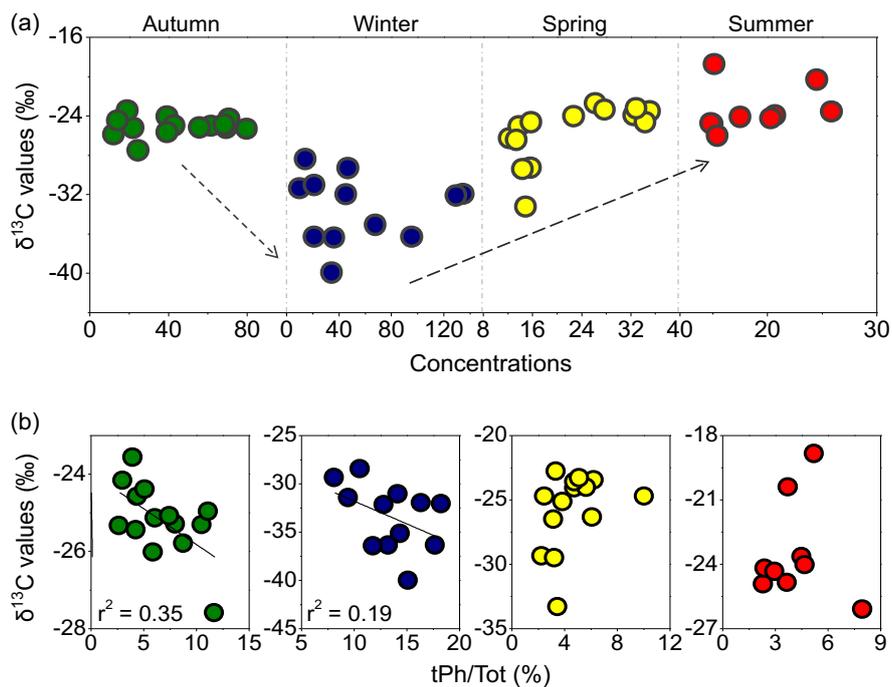
998 **Figure 8.** (a) Seasonal variations in the stable carbon isotope ratios ($\delta^{13}\text{C}$) of C_2 , (b)

999 correlations between $\delta^{13}\text{C}$ values of C_2 and relative abundances of oxalic acid to total diacids

1000 (C_2/Tot) in $\text{PM}_{2.5}$ in Beijing. The black dotted lines represent the average $\delta^{13}\text{C}$ values.

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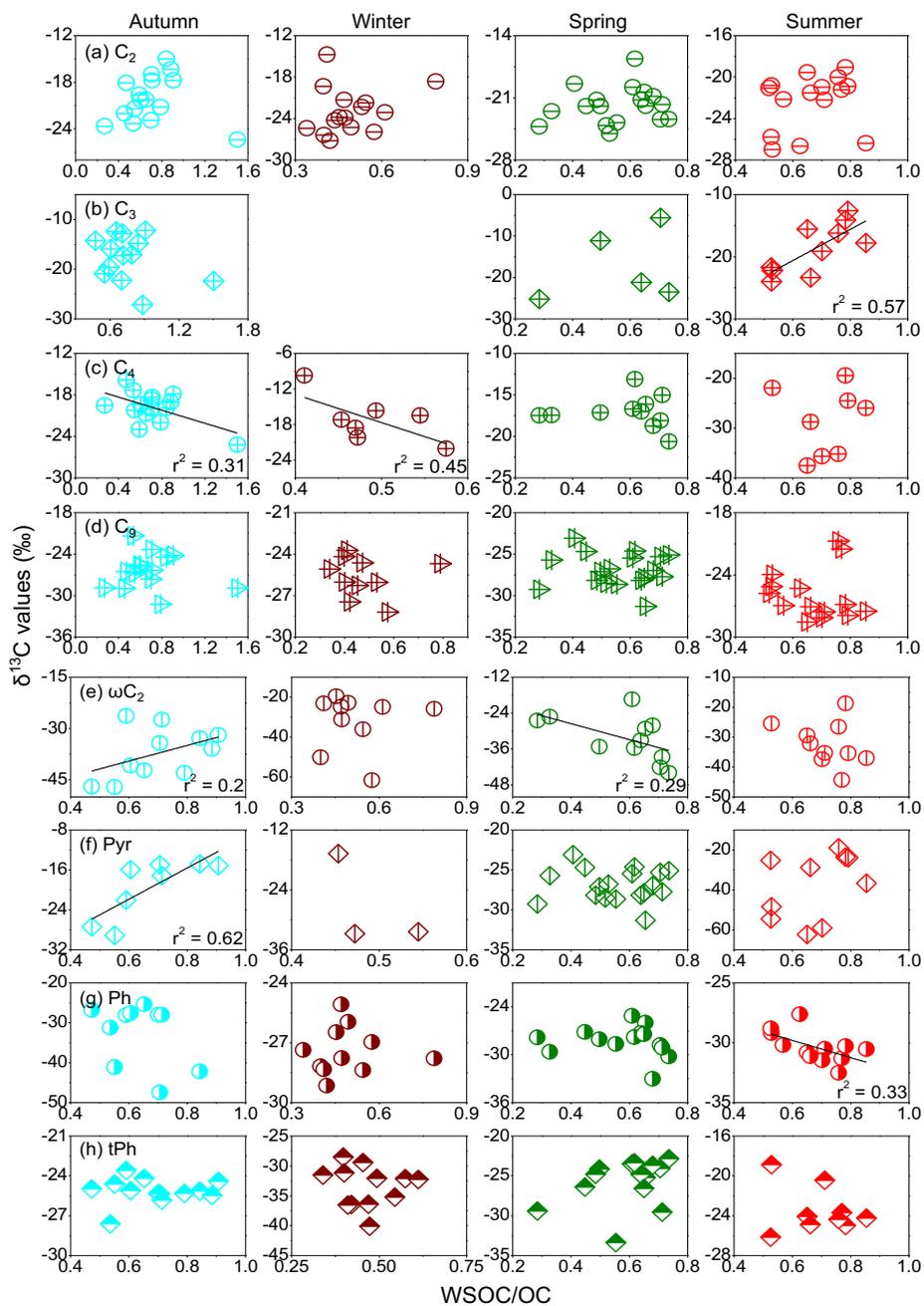


1003

1004

1005 **Figure 9.** (a) Seasonal variations in stable carbon isotope ratios ($\delta^{13}\text{C}$) of tPh, (b) correlations
1006 between the $\delta^{13}\text{C}$ values of tPh and relative abundances of terephthalic acid to total diacids
1007 (tPh/Tot) in $\text{PM}_{2.5}$ in Beijing.

1008



1009

1010

1011 **Figure 10.** Correlations between compound-specific stable carbon isotope ratios of selected

1012 diacids and oxoacids and WSOC/OC ratios in PM_{2.5} in Beijing.