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

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Abstract

This study investigates the seasonal variation, molecular distribution and stable carbon isotopic composition of diacids, oxocarboxylic acids and α-dicarbonyls to better understand the sources and formation processes of fine aerosols ($PM_{2.5}$) in Beijing. The concentrations of total dicarboxylic acids varied from 110 to 2580 ng m^{-3}, whereas oxoacids (9.50–353 ng m^{-3}) and dicarbonyls (1.50–85.9 ng m^{-3}) were less abundant. Oxalic acid was found to be the most abundant individual species, followed by succinic acid or occasionally by terephthalic acid (tPh), a plastic waste burning tracer. Ambient concentrations of phthalic acid (37.9±27.3 ng m^{-3}) and tPh (48.7±51.1 ng m^{-3}) were larger in winter than in other seasons, illustrating that fossil fuel combustion and plastic waste incineration contribute more to wintertime aerosols. The year-round mass concentration ratios of malonic acid to succinic acid (C_3/C_4) were relatively low by comparison with those in other urban aerosols and remote marine aerosols. The values were less than or equal to unity in Beijing, implying that the degree of photochemical formation of diacids in Beijing is insignificant. Moreover, strong correlation coefficient of major oxocarboxylic acids and α-dicarbonyls with nss-K^+, suggest biomass burning accounting for a large contribution to these organic acids and related precursors. The mean $\delta^{13}C$ value of succinic acid is highest among all species with values of –17.1±3.9‰ (winter) and –17.1±2.0‰ (spring), while malonic acid is less enriched in ^{13}C than others in autumn (–17.6±4.6‰) and summer (–18.7±4.0‰). The $\delta^{13}C$ values of major species in Beijing aerosols are generally lower than those in the western North Pacific atmosphere, the downwind region, which indicates that $\delta^{13}C$ values of diacids depend on their precursor sources in Beijing. Therefore, our study demonstrates that in addition to photochemical oxidation, high abundances of diacids, oxocarboxylic acids and α-dicarbonyls in Beijing are largely associated with anthropogenic primary emissions, such as biomass burning, fossil fuel combustion, and plastic waste burning.

1 Introduction

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

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

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

Realizing the physical and chemical characteristics of organic matters is vital for determining the source regions and elucidating the mechanism of evolution of air pollution events. Various measurements have been employed for closer acquaintances of the sources, transformation and long-distance transport of organic compounds, including studies on sugars, unsaturated fatty acids, *n*-alkanes and *n*-alcohol, along with aromatic hydrocarbons (Kawamura and Gagosian, 1987; Kawamura et al., 1996a). Zhang et al. (2010) conducted field observations of dicarboxylic acids and pinene oxidation products with a model analysis of the temperature dependencies of emissions, gas-particle partitioning, and chemical reactions. Furthermore, the analyses of stable carbon isotope ratios of water-soluble organic acids can be effectively applied to assessing the photochemical aging level and relative contributions of primary emissions to aerosol samples in atmosphere using the estimated kinetic isotope effect of target compound with OH radical (Kawamura and Watanabe, 2004; Wang and Kawamura, 2006; Kawamura and Bikkina, 2016). With this approach, it is possible to differentiate between the impacts of local sources and long-range transported air masses.

Beijing, the capital of China, is located on the northwest rim of the North China Plain and is surrounded by industrialized areas from the southwest to the east. Emissions from local and regional sources potentially undergo photochemical processes in the course of transport by means of prevalent winds, which influence the atmospheric visibility and quality in Beijing (Xia et al., 2007). Several studies have reported that the source strength in Beijing is characterized by fossil fuel combustion in winter, whereas it is characterized by secondary aerosol formation in summer (Lin et al., 2009; Sun et al., 2015; Wang et al., 2006a). Ji et al. (2016) observed increasing photochemical activity in autumn and winter, and he noted biomass burning as a substantial pollution factor in Beijing. In addition to the studies on long-term observations of organic aerosols, specific haze pollution episodes occurring in Beijing have been investigated. For example, Huang et al. (2014) concluded that in comparison with secondary sources, primary emissions contributed slightly less to fine particles in haze events at urban locations in China, including Beijing, using both molecular markers and radiocarbon (^{14}C) measurements. To ascertain the influential factors for air quality in Beijing, two studies demonstrated that besides motor exhaust, oxidation pathways of organic species is also critical (Ho et al., 2015; Ho et al., 2010). Although such studies have focused on the characterization of organic aerosols in Beijing at a molecular level, long-term analyses of low molecular weight (LMW) dicarboxylic acids, oxoacids and α-dicarbonyls with their stable carbon isotopic compositions have not been investigated.

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

2 Experimental section

2.1 $PM_{2.5}$ sampling

The sampling site is situated on the rooftop of a building (8 meters above ground level) in the Institute of Atmospheric Physics (39°58’28’’N, 116°22’16’’E), which is considered as a representative urban site in Beijing (Sun et al., 2012). $PM_{2.5}$ samples were collected onto pre-heated (450°C, 6 hours) quartz-fiber filters (Pallflex) by using a high-volume air sampler (TISCH, USA) at an airflow rate of 1.0 m^3/min for 23 h from September 2013 to July 2014 (n=65). Field blanks were prepared before, during and after the campaign by putting the pre-combusted filter onto the sampler for a few minutes without pumping. After sampling, the filters were properly stored at −20°C to avoid microbial degradation of organics and evaporation of semi volatile components. Beijing is surrounded by Hebei Province and Tianjin Municipality with intensely developed industries (Xia et al., 2007), so the atmospheric visibility and quality in Beijing are sometimes seriously deteriorated owing to the substantial primary aerosols from these areas.

2.2 Analytical procedures

Aerosol samples were analyzed for diacids and related compounds using a method reported previously (Kawamura and Ikushima, 1993; Kawamura, 1993). In brief, water-soluble organic acids were obtained from ultrasonic extraction for small discs of $PM_{2.5}$ samples merged in Milli-Q water for 3 times. Then, the sample extractions were concentrated into dryness and further reacted with 14% BF_3/*n*-butanol. Finally, the derivatized extracts were dissolved in *n*-hexane and analyzed by a split/splitless Agilent 6980GC/FID equipped with HP-5 column (0.2 mm × 25 m, 0.5 μm film thickness). The field blank filters were also used same procedures to analyze. Concentrations of the target organic acids in this study were corrected for the field blanks. Furthermore, recoveries of major organic acids of this method were better than 85%.

2.3 Measurement of isotopic compounds

Determination of stable carbon isotope ratio ($\delta^{13}C$) values for LMW organic acids relative to Pee Dee Belemnite (PDB) were used the technique set up previously (Kawamura and Watanabe, 2004). In short, some internal standard (n-alkane C_{13}) was added into derivatized fraction of each sample at a proper proportion. $\delta^{13}C$ values of the derivatized dibutyl esters or dibutoxy acetals, measured using GC (HP6890)/isotope ratio mass spectrometer (irMS), were then calculated for diacids, ketoacids and α-dicarbonyls based on the isotopic mass balance equation. Each aerosol sample was analyzed for several times to make sure that the differences for major diacids in $\delta^{13}C$ below 1‰ in general. But as to few compounds, the analysis differences were less than 2‰.

2.4 Inorganic ions, WSOC, OC and EC measurements

A part of each filter was extracted with 20 ml of Milli-Q water under ultrasonication for 30 minutes and passed through a filter head of 0.22 μm nominal pore size (PVDF, Merck Millipore Ltd). Ion chromatography (ICS-2100) was used to determine the concentrations of cations (Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}). The separation of cations was accomplished by using an IonPac CS 12A (4×250 mm) analytical column, with an eluent flow rate of 1.0 ml/min. Another ICS-2100 system was used to measure the concentrations of anions (F^-, Cl^-, NO_3^-, and SO_4^{2-}). The separation of anions was accomplished using an IonPac AS11-HC analytical column. The eluent was 25.0 mM KOH at a flow rate of 1.0 ml/min. The anions and cations were analyzed separately after the extraction solution was divided into two paths.

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

2.5 Air mass backward trajectories

To better evaluate the influences of air masses from different origins on organic aerosols in Beijing, 5-day backward trajectory analyses with fire spots were performed for each sample from the sampling site at a height of 500 m (a.s.l.) by using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT4) mode (Rolph, 2011, 2003). Burning activities in East Asia were illustrated by fire spots, and the datasets were downloaded from MODIS website (https://firms.modaps.eosdis.nasa.gov/download/request.php). The backward trajectories were assorted into several major classifications on the basis of prevalent winds direction. And the numbers in each panel implied the percentages of hourly trajectories in the sampling season to better illustrate the air mass origins, as given below in this study (Fig. 1).

3 Results and discussion

3.1 Molecular distribution

Table 1 summarizes the seasonal concentrations of LMW diacids (C_2–C_{12}), oxocarboxylic acids (ωC_2–ωC_9, pyruvic acid), and α-dicarbonyls (C_2–C_3) in $PM_{2.5}$ particles in Beijing. Oxalic acid (30.8–1760 ng m^{-3}, average 288 ng m^{-3}) was the predominant individual diacid, showing a peak in autumn and a minimum in winter, whereas its relative abundances (0.39–0.58, average 0.52) to total measured diacids exhibited a maximal and a minimal ratio in summer and wintertime, respectively (Table 3). The predominance of C_2 found in this study was coincident with the results of terrestrial and marine particles in previous studies (Ho et al., 2007; Pavuluri et al., 2010; Kawamura and Yasui, 2005; Fu et al., 2013; Kawamura and Bikkina, 2016). Among ω-oxocarboxylic acids (ωC_2–ωC_9), glyoxylic acid (ωC_2) was detected as the dominant oxoacid.

Either succinic acid (C_4) or occasionally tPh was the second most abundant compound, followed by ωC_2 in cold seasons (autumn and winter) or malonic acid (C_3) in warm seasons (spring and summer). Total diacids showed the largest abundance in autumn, followed by spring, whereas total oxoacids and α-dicarbonyls both displayed higher levels in cold seasons, especially in autumn (Table 1). The concentrations of individual dicarboxylic acid reduced along with the increase of carbon numbers, but in the range of longer-chain diacids (C_6–C_{12}), adipic (C_6) and azelaic (C_9) acids showed more abundances than other species in the atmosphere throughout the year (Fig. 2).

3.2 Seasonal variations

Seasonal trends of homologues series of diacids and other main species presented three different patterns. The first type, such as oxalic, malonic, succinic, adipic acids and methylglyoxal (MeGly), showed maximum concentrations in autumn with relatively high abundances in late spring to early summer. The second type showed maximum concentrations in cold seasons (autumn, winter): phthalic, terephthalic and glyoxylic acid peaked in winter, while azelaic acid (C_9), glyoxal (Gly), methylmaleic (mM), maleic (M) and fumaric (F) acids peaked in autumn. For the third type, concentrations of methylmalonic (iC_4) and 2-methylglutaric (iC_6) acids were almost constant throughout the sampling year. These three seasonal trends indicated different emission sources of the compounds and their precursors and evolution processes of organic aerosols in the atmosphere.

Total concentrations of diacids showed a wide range (110–2580 ng m^{-3}) with an average maximum (763 ng m^{-3}) and minimum (366 ng m^{-3}) in autumn and winter, respectively. These values were comparable to those in Tanzania, East Africa (wet season: 329 ng m^{-3}; dry season: 548 ng m^{-3} in $PM_{2.5}$) (Mkoma and Kawamura, 2013), slightly lower than those in Tokyo, Japan (726 ng m^{-3} in June, 682 ng m^{-3} in July, and 438 ng m^{-3} in November) (Kawamura and Yasui, 2005), and Gosan, Jeju Island in Korea (735 ng m^{-3} in spring, 784 ng m^{-3} in summer, 525 ng m^{-3} in autumn, and 500 ng m^{-3} in winter) (Kundu et al., 2010b). The comparisons of the diacids in Beijing with those in other urban cities are presented in Table 2.

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

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

Azelaic acid was observed in abundance throughout the whole sampling period, while the monthly mean ratios of C_9 to total diacids (C_9/Tot) ranged from 0.05 to 0.09, with the highest values in winter (Table 3). Kawamura and Kaplan (1987) reported that C_9 can be detected in motor exhaust and may originate from the oxidation of corresponding hydrocarbons, suggesting that dicarboxylic acids are combustion products of normal alkanes in fuels. A great deal of chloride in wintertime is linked to increased emissions of coal incineration in Beijing, particularly under stagnant meteorological conditions that facilitate the formation of particle-phase ammonium chloride (Sun et al., 2013a). Azelaic acid correlated well with K^+ ($0.3 \le r^2 \le 0.4$), a tracer for biomass burning (Andreae, 1983), and Cl^- ($0.4 \le r^2 \le 0.5$) in cold seasons (Fig. S1), indicating that substantial amounts of C_9 may be stemmed from the local and surrounding combustion activities in Beijing.

Ph and tPh are both more abundant in cold seasons than in warm seasons. We found Ph to be the fourth most abundant species in winter (37.9±27.2 ng m^{-3}) and summer (24.9±8.2 ng m^{-3}). Concentration ranges of Ph (7.6–98.5 ng m^{-3}, mean: 31.7 ng m^{-3}) in cold seasons were larger than those (0.08–7.47 ng m^{-3}, mean: 1.76 ng m^{-3}) from Gosan, Jeju Island (Kundu et al., 2010b), but were obviously lower than these (53–278 ng m^{-3}, mean: 150 ng m^{-3}) in urban Xi’an (Cheng et al., 2013). Phthalic acid is either formed via photochemical pathways of naphthalene, or directly released into air by fossil fuel burning and the incomplete combustion of aromatic hydrocarbons in motor vehicles. Moreover, the abundance of Ph may also be caused by increased phthalates emissions from plastic waste burnings in heavily polluted areas in China (Deshmukh et al., 2015). Phthalic acid esters are used as plasticizers in resins and polymers (Simoneit et al., 2005). Therefore, anthropogenic emissions contributed to relatively high concentrations of Ph in $PM_{2.5}$ in Beijing.

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

Oxocarboxylic acids, which are understood as the intermediate products of the oxidation of mono-carboxylic acids, can further be photochemically oxidized to form diacids (Warneck, 2003; Carlton et al., 2007). Concentrations of all ketoacids varied from 9.50 to 353 ng m^{-3} during sampling periods with a maximum (73.3±76.3 ng m^{-3}) in autumn and a minimum (46.5±26.8 ng m^{-3}) in summer. Except for ωC_7 and ωC_8, the oxoacids showed larger concentrations in cold seasons (autumn and winter), which might be attributed to accumulation under stagnant meteorological conditions. Their concentrations were higher than those in aerosols from Tanzania (60.0±19.0 ng m^{-3} and 31.0±18.0 ng m^{-3} in $PM_{2.5}$ during dry and wet seasons, respectively) (Mkoma and Kawamura, 2013) but much lower than these detected in Mangshan, a rural site in Beijing (159 ng m^{-3} in daytime, 97.9 ng m^{-3} in nighttime) (He et al., 2014).

Glyoxylic acid (ωC_2) is measured as the most abundant oxoacid, followed by pyruvic (Pyr) and 4-oxobutanoic (ωC_4) acids. All of them are important intermediates in photooxidation processes for the production of low carbon-numbered diacids such as C_2, C_3 and C_4 diacids (Hatakeyama et al., 1987). ωC_2 and Pyr are more abundant in cold seasons (Table 1) with similar seasonal patterns (Fig. 3g–h). Both correlated well with K^+ (Fig. S2) and Cl^- (Fig. S3) in sampling seasons. These connections demonstrate that ωC_2 and Pyr originated from common combustion emissions or similar secondary formation pathways. 9-Oxononanoic acid (ωC_9), photochemically generated from unsaturated fatty acids (Kawamura and Gagosian, 1987), showed larger concentrations in autumn and winter. This concentration trend was consistent with that of azelaic acid. Additionally, a lower thermal inversion layer, less precipitation and a slower wind speed can enhance the accumulation of organic compounds.

Total concentrations of α-dicarbonyls varied with a wide range (1.50–85.9 ng m^{-3}) and were relatively more abundant in cold seasons (25.1±28.1 ng m^{-3} in autumn, 15.5±15.9 ng m^{-3} in winter). And the average seasonal concentrations are larger than those at Gosan, Jeju island in South Korea (Kundu et al., 2010b). Two α-dicarbonyls (glyoxal and methylglyoxal) are semi-volatile gaseous organic precursors produced by oxidation of isoprene (Zimmermann and Poppe, 1996), monoterpenes (Fick et al., 2004) and other biogenic volatile organic compounds (VOCs) (Ervens et al., 2004) and anthropogenic aromatic hydrocarbons (e.g., benzene and toluene) (Volkamer et al., 2001). Both carbonyls can form less volatile organic polar acids including Pyr and ωC_2 in subsequent oxidation processes, which are key intermediates to produce oxalic acid (C_2). Glyoxal (Gly) and methylglyoxal (MeGly) 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 year (Fig. S2), whereas Gly and MeGly showed good relations with Cl^- (Gly: $0.3 \leq r^2 \leq 0.8$, $0.4 \leq r^2 \leq 0.8$) in autumn, winter and summer (Fig. S3). Concentrations of these two carbonyls are largely affected by biogenic precursors (e.g., isoprene and monoterpenes) emitted from vegetation and biomass burning activities during entire sampling periods in addition to coal burning and motor exhaust (aromatic hydrocarbons). Low temperature is favorable for the adsorption and condensation of gaseous organic species on existing particles in cold seasons.

3.3 Correlation analysis and seasonal variations of concentration ratios

The ratio of oxalic acid to total diacids (C_2/Tot) has been applied to estimate the relative contribution of secondary fraction to atmospheric aerosols during long-range transport. Typically, higher mass concentration ratios are associated with more aged aerosols

(Kawamura and Sakaguchi, 1999). As for water-soluble organic acids in this paper, the ratios of C_2/Tot were the lowest in winter (0.39±0.05) (Table 3), indicating that wintertime organic aerosols may be less aged (Fig. 4a). After the main emission of $PM_{2.5}$ particles from motor vehicles, fossil fuel and biomass burning activities from local regions in winter, the aging process might occur during atmospheric transport. In contrast, C_2/Tot ratios are similar in the other three seasons (Table 3). In total, the seasonal mean values of C_2/Tot in this study were lower than the winter ratio values (0.8±0.04) in Central Himalayan owing to the aging of organic compounds occurring in the northerly wind, but were close to those in summer (0.5±0.01) due to increased temperature and high wind in the Central Himalayas (Hegde and Kawamura, 2012). Thus, the ratios of C_2/Tot and this seasonal trend indicate that the photochemical formation of dicarboxylic acids is insignificant in urban Beijing.

Two pathways for the generation of C_2, C_3 and C_4 diacids in air were reported by Kawamura et al. (1996a). On the one hand, C_4 diacid can be generated via the photooxidation of unsaturated fatty acids from terrestrial higher plants and domestic cooking over continental lands, as well as from phytoplankton emissions over the remote marine regions (Kawamura and Sakaguchi, 1999; Kawamura and Bikkina, 2016), and subsequently be oxidized to form C_3 and C_2 diacids (Kawamura and Ikushima, 1993). Typically, concentrations of C_2, C_4 and C_9 diacids showed similar seasonal variation trends (Fig. 1), implying that they were derived from common primary emissions or photochemical processing. Furthermore, C_2/Tot (C_2%) showed strong correlations with C_2/C_4 in all four seasons (Fig. S4), indicating the importance of biogenic unsaturated fatty acids, followed by secondary formation ways. On the other hand, aromatic hydrocarbons may be oxidized to produce Gly and ωC_2, which are intermediates in the formation of C_2 (Kawamura and Bikkina, 2016; Kawamura and Ikushima, 1993). Biogenic and anthropogenic VOCs (e.g., isoprene) can react with oxidants to generate Gly and MeGly in the gas phase. Hydrated α-dicarbonyls can ultimately produce C_2 via the photochemical oxidation of Pyr and ωC_2 as intermediates (Lim et al., 2005), whereas C_3 and C_4 diacids cannot be produced in this way.

We, therefore, would like to investigate the importance of these formation pathways by examining the interrelationships between concentration ratios of C_2/Pyr, $C_2/\omega C_2$, C_2/Gly and

C_2/Tot in this study. Relative high ratios of C_2/Pyr, C_2/ωC_2 and C_2/Gly were observed in autumn, spring and summer (Fig. 4c-e), but their values were much lower than those detected in particulate matters at Gosan, Jeju Island (Kundu et al., 2010b), where the aerosols were relatively aged during long-range transport. Figure S4 shows that strong relationships between C_2/ωC_2, C_2/Pyr and C_2/Tot (%) only existed in summer. No correlation was observed between C_2/Gly and C_2/Tot (%). A negative correlation between C_2/ωC_2 and C_2/Tot (%) in summer, has never been reported before. These phenomena demonstrate that abundant C_2, ωC_2, Pyr, and Gly were emitted directly from extensive agricultural residue burnings, motor vehicles and fossil fuel burning in the studied regions (Fig. 1). The supplement of ωC_2, Pyr, and Gly is faster than their photodegradation to form C_2 in air. Only slightly stronger photochemical production of C_2 from Pyr was observed in summer.

C_3 diacid can be produced as a result of hydrogen abstracted by OH radicals, followed by decarboxylation processing of C_4 diacid (Kawamura and Ikushima, 1993). The mass concentration ratio of C_3/C_4 is a good indicator for evaluating the contributions of dicarboxylic acids from primary emissions or secondary oxidation production in the atmosphere (Kawamura and Sakaguchi, 1999). Lower C_3/C_4 ratios were detected in vehicular exhaust by Kawamura and Kaplan (1987), ranging from 0.25 to 0.44 with an average of 0.35. Less thermally stable C_3 diacid can degrade more preferentially to other species rather than remaining stable during incomplete combustion processes.

Figure 4b shows that the C_3/C_4 ratios were relatively larger in the warm seasons (spring & summer). However, the temporal trend of the C_3/C_4 ratios is relatively flat throughout the sampling year, and most values are less than or equal to unity in Beijing. Low C_3/C_4 ratio is associated with the substantial emissions from motor vehicles (Kawamura and Kaplan, 1987). On the contrary, the prolonged secondary oxidation of organic matters leads to C_3/C_4 values much greater than unity (Kawamura and Ikushima, 1993; Kawamura and Sakaguchi, 1999). The ratios of C_3/C_4 reported in this study are lower than that (one-year average of 1.49) in urban Tokyo (Kawamura and Ikushima, 1993) and in the remote Pacific Ocean (average 3) (Kawamura and Sakaguchi, 1999), where dicarboxylic acids are largely produced by photooxidation reactions. These results demonstrated that in addition to slightly enhanced atmospheric photochemical reactions in summer, incomplete combustions, like motor vehicles and biomass burnings, overwhelmingly contributed to dicarboxylic acids in Beijing.

Phthalic acid (Ph) was one of the most abundant compounds during the sampling period. The seasonal trends of phthalic acid to total dicarboxylic acids (Ph/Tot) are shown in Figure 4h. The Ph/Tot ratios in winter were nearly 2–3 times greater than those in spring and autumn. These findings imply that phthalic acid is largely emitted by anthropogenic sources in winter, mainly as a result of intensive coal burning for house heating. It is worth noting that Ph/Tot ratio was also relatively high in summer. Previous study reported that a great amount of naphthalene obtained in Beijing is an important raw material for the substantial formation of phthalic acid (Liu et al., 2007). Therefore increased ambient temperatures and stronger solar radiation in summertime facilitate the transformation of gaseous PAHs (e.g., naphthalene) to produce relative high levels of Ph in Beijing.

C_6 and Ph can be formed via secondary oxidations of anthropogenic cyclic olefins (e.g., cyclohexene) and aromatic hydrocarbons, respectively, whereas C_9 is mainly produced by photochemical oxidation of biogenic unsaturated fatty acids (Kawamura and Gagosian, 1987; Kawamura and Ikushima, 1993). Thus, the mass concentration ratios of C_6/C_9 and Ph/C_9 may effectively indicate the source strength of anthropogenic and biogenic emissions to these organic acids.

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

Maleic acid (M), originated predominantly from photochemical oxidation of aromatic hydrocarbons (e.g., benzene and toluene), can be subsequently isomerized to its *trans*-isomer, fumaric acid (F), under favourable conditions. Lower M/F values have been detected in atmospheric aerosols over the North Pacific Ocean (0.3) (Kawamura and Sakaguchi, 1999) as well as at Alert in the high Arctic (ratio range: 0.5–1.0) (Kawamura et al., 1996a). The M/F ratios are almost constant in winter (2.0±0.66) and spring (2.0±0.67) and are higher than those in autumn (1.67±0.81) and summer (1.35±0.49). This trend may be associated with substantial amounts of precursors emitted from biomass burning in autumn, fresh aerosols brought by high-speed wind in spring and enhanced isomerization reaction from M to F under intense solar radiation in summer. The conversion of maleic to fumaric acids can be restrained in polluted environments with minimum weak sunlight (Kundu et al., 2010a). Therefore, M may not be effectively isomerized to F during wintertime in Beijing. Though M/F obtained the lowest ratio values in summer, dicarboxylic acids and related compounds in Beijing are not seriously subjected to secondary oxidation process in the whole year with comparison to the strength of primary emissions.

Based on field observations, Kawamura and Ikushima (1993) hypothesized that C_4 diacid can transform into malic acid (hC_4) by means of hydroxylation. The hC_4/C_4 ratios were the highest in warm seasons (0.04±0.01 in summer, 0.03±0.02 in spring), which supported this hypothesis. hC_4/C_4 ratios in summer are 2–4 times larger than those in cold seasons, similar to the trends observed in Jeju Island, Korea (Kundu et al., 2010b) and urban Tokyo (Kawamura and Ikushima, 1993).

3.4 Comparisons of the mean mass ratios between sampling sites

To assess the emission strength of anthropogenic activities in Beijing, the mean values of (a) C_3/C_4, (b) M/F, (c) Ph/C_9, (d) Ph/Tot and (e) tPh/Tot mass ratios were compared with those in other sampling sites, including Xi'an (Wang et al., 2012), Gosan, Jeju Island (Kundu et al., 2010b) and the western Pacific Ocean (Wang et al., 2006b). Xi'an, a megacity in the Guanzhong Plain, is located in one of the regions heavily polluted by fossil fuel and biofuel combustion. Atmospheric aerosols at the Gosan site are mixtures of westerly winds from high latitude regions of Eurasia. Marine aerosols over the western Pacific Ocean are a combination of long-range transported continental aerosols and locally emitted marine aerosols.

Figure 5 presents the global distribution of diagnostic mass ratios of diacids and related compounds. Rather low C_3/C_4 ratios were observed in urban aerosols, including Beijing and Xi'an, compared to those aged organic matters collected from Gosan, Jeju Island and the western Pacific Ocean. Similarly, larger C_3/C_4 ratios were obtained in summer than in the other seasons. The same observation in Beijing may be attributable to the enhancement of secondary oxidation that favors the conversion of C_4 diacid to C_3 diacid in the warm season; however, in that case, the photochemical activity is insignificant compared to the primary emissions. Similar to the C_3/C_4 ratios, low M/F ratios indicate the importance of photochemical reaction routes (Kawamura and Sakaguchi, 1999). The mean values of M/F in the Beijing aerosols are larger than or comparable to those reported in Gosan, Jeju Island (spring: 1.38, summer: 0.76, autumn: 1.62, and winter: 2.21) but lower than those obtained in Xi'an aerosols (summer: 2.22 and winter: 2.38), indicating that the $PM_{2.5}$ aerosols in Beijing are mainly linked with regional primary emissions, whereas the photo-isomerization from *cis* to *trans* isomer is insignificant.

Usually, high Ph/C_9 ratios were detected in continental samples owing to a relatively strong contribution from anthropogenic sources to dicarboxylic acids. A bit larger values of Ph/C_9 (in average) were obtained in Xi'an than those in Beijing because the air masses in Xi'an were more heavily influenced by intense industrial emissions. Although the values of Ph/C_9 in both megacities were higher than those in the western Pacific Ocean, the wintertime Ph/C_9

ratios in Gosan were much greater than those in Beijing, which may be caused by the secondary generation of abundant precursors, such as naphthalene, which were transported by long-distance from East Asia.

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

3.5 Source identification by principal component analysis

Previous studies have utilized principal component analysis (PCA) to discriminate the source apportionment of atmospheric aerosols (Hopke, 1985). In this paper, typical dicarboxylic acids with other major components were chosen for factor analysis. Compounds with common sources or photooxidation reactions would be likely to display similarities in mass variations and be assorted into one "factor". High loadings of variables on the selected species reveal closer links of sources and formation pathways between these compounds (Wu et al., 2015). Here, "total varimax" maximizes the variance of the squared elements in the columns of a factor matrix. The PCA result for dicarboxylic acids and other main components in $PM_{2.5}$ in Beijing from Sep. 2013 to Jul. 2014 is given in Table 4.

During the whole sampling period, the first factor accounted for 75.2% of the total variance with high loadings of selected diacids, WSOC, and EC (a tracer for incomplete combustion-generated carbon emissions). Typically, the prolonged photochemical oxidation of organics in the atmosphere leads to enhanced concentrations of polar organic matters. WSOC can account for 45–75% of aerosol carbon mass in biomass burning emissions (Falkovich et al., 2005) and 20–60% of that in fossil fuel combustion-derived particles (Pathak et al., 2011). Agricultural waste burning is a substantial pollution factor in Beijing

(Fig. 1) (Viana et al., 2008; Cheng et al., 2014), especially in late June and early October, resulting in substantial organic aerosols (Fu et al., 2012). In many studies, open-waste burning are clubbed with biomass and fuel burning aerosols (Akagi et al., 2011; Lei et al., 2012). C_4, C_9, tPh, ωC_2, Pyr, Gly and MeGly showed strong correlations in the first factor, implying that burning activities contribute to a large fraction of their concentrations, including biomass burning, biofuel combustion and burning of municipal wastes. For example, the photooxidation of *p*-xylene, a main precursor of terephthalic acid dimethyl ester, can produce glyoxal (Simoneit et al., 2005; Kawamura and Pavuluri, 2010; Volkamer et al., 2001).

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

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

3.6 Stable carbon isotopic compositions

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

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

The mean seasonal $\delta^{13}C$ values of C_9 varying from –25.6‰ to –26.9‰ were smaller than those of C_2–C_4 diacids. It's noteworthy to state that more depletion of ^{13}C in continental higher plants (C_3 plants: –27‰) is in comparison with the particulate organic matters from marine plankton activities (around: –20‰) (Miyazaki et al., 2010; Turekian et al., 2003). The $\delta^{13}C$ values of azelaic acid suggested that unsaturated fatty acids derived from biomass burnings in the surrounding areas is a key source of C_9 in Beijing.

As mentioned earlier, Ph is mainly formed via the photochemical processes of polycyclic aromatic hydrocarbons, but it can be emitted directly from fossil fuel combustion as well (Kawamura and Kaplan, 1987; Fraser et al., 2003). The largest $\delta^{13}C$ value of Ph in winter was linked with its peak concentrations. This finding may be ascribed to the intensity of coal and gasoline combustion in Beijing, especially the stagnant atmospheric conditions in favor of accumulation of organic matters during wintertime (Cao et al., 2011). In general, the organic aerosols derived from coal and gasoline burnings are more enriched in ^{13}C than other emissions, including diesel combustion, aerosols released from C_3-plants, and secondary organic matters.

For terephthalic acid, the lowest $\delta^{13}C$ value of tPh (ave: –33.5‰) in winter supports the finding that it is directly emitted from the burning of plastic wastes. Waste burning usually contains many plastics and occurs frequently in open spaces without emission control

(Kawamura and Pavuluri, 2010), in addition to other local anthropogenic emissions. Lighter $\delta^{13}C$ values of major compounds in Beijing than those in the marine and Arctic areas may be explained by more contributions of primary emissions from anthropogenic sources.

Box plots of stable carbon isotope ratios ($\delta^{13}C$ values) are displayed in Fig. 6 for seasonal distributions of diacids, glyoxylic and pyruvic acids in $PM_{2.5}$. The $\delta^{13}C$ values of oxalic acid ranged from –27.2‰ to –14.8‰ in sampling time, with similar seasonal mean $\delta^{13}C$ values. Malonic acid was more enriched in ^{13}C than others in autumn (–17.6‰) and summer (–18.7‰), while succinic acid showed the heaviest $\delta^{13}C$ value (–17.1‰) among all species in winter and spring. A previous study noted that increasing concentrations of oxalic and malonic acids inhibit the growth of total fungi number due to the lower pH, which in turn changes the efficiency of fungi to degrade the malonic acid (Côté et al., 2008). Hence, an enrichment of ^{13}C in remaining malonic acid may be interpreted by the isotopic fractionations occurring in the breakdown ways of dicarboxylic acids or photochemical degradation of C_3 diacid (Pavuluri and Kawamura, 2012). In this study, the median $\delta^{13}C$ values of ωC_2 were much lower than those of C_2 in all seasons, whereas $\delta^{13}C$ of Pyr showed median values similar to C_2 in autumn and spring, which are surprisingly higher than that of C_2 in autumn.

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

In order to further estimate the impacts of air mass source regions on $\delta^{13}C$ values of specific compounds, five-day backward trajectories for each aerosol sample are illustrated in Figure 1. Data from urban Sapporo (Aggarwal and Kawamura, 2008), Gosan of the Jeju Island (Zhang et al., 2016) and remote marine regions (Wang and Kawamura, 2006c) are plotted together with the seasonal mean $\delta^{13}C$ values of major species detected in this study (Fig. 7). The largest average $\delta^{13}C$ value of oxalic acid was observed in the Gosan samples. The seasonal mean $\delta^{13}C$ values of malonic acid in Beijing were higher than those in Sapporo and remote marine areas, but C_3 was less enriched in ^{13}C compared to Gosan owing to the degradation of C_3 diacid or C_2 diacid depleted in ^{13}C. The mean $\delta^{13}C$ values of succinic acid are comparable to those in the other three places, except for summer. The mean $\delta^{13}C$ values of Pyr in autumn (–19.6‰) and spring (–22.3‰) were similar to the data in Sapporo (–20.3‰) and Gosan (autumn: –19‰, winter: –22.2‰, spring: –19.1‰, summer: –17.6‰) aerosols. The δ^{13}C values of ωC_2 and Ph in remote marine samples are the highest, followed by those for Sapporo and Gosan sites and then Beijing. In contrast, the seasonal mean δ^{13}C values of C_6 and C_9 in Beijing are similar to those in Sapporo and Gosan aerosols but lower than those in marine aerosols.

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

3.8 Relations between δ^{13}C values and photochemical aging

C_2/Tot ratio is suggested to be a useful tracer to evaluate the aging of atmospheric aerosols (Kawamura and Sakaguchi, 1999). The mean δ^{13}C values of oxalic acid showed the smallest value in winter (–22.9‰) and the highest value in autumn (–20.1‰), followed by spring (–21.9‰) (Fig. 8a). Here, we compared the δ^{13}C values of C_2 and its concentration changes with the relative abundance of C_2 to total diacids (Fig. 8b). The isotopic ratio values of C_2 were positively correlated with C_2/Tot ratios in autumn (r^2 = 0.45) and winter (r^2 = 0.29), suggesting that production of C_2 from the oxidation of precursors can contribute to the increase of δ^{13}C values (Pavuluri et al., 2011). Due to enhanced primary emissions from coal combustion and biomass burning, stagnant atmospheric inversion can favor the accumulation of pollutants. Furthermore, the $\delta^{13}C$ values of tPh decreased from autumn to winter, followed by an increase toward summer (Fig. 9). Seasonal $\delta^{13}C$ values of tPh decreased with the enhanced ratios of tPh to total diacids (tPh/Tot) in autumn ($r^2 = 0.35$) and winter ($r^2 = 0.19$), indicating large emissions from municipal waste burning activities in cold seasons, especially in winter.

Aged organic aerosols are characterized by high abundance of polar and water-soluble organic species, leading to high values of WSOC/OC ratio. However, in the Beijing samples, the $\delta^{13}C$ values of major species (C_2, C_3, C_4, C_9, ωC_2, Pyr, Ph and tPh) did not show strong relationships with the WSOC/OC ratios in this paper (Fig. 10). The $\delta^{13}C$ values of C_3 only correlated well with the WSOC/OC ratios in summer ($r^2 = 0.57$), in conformity with the variation of C_3/C_4 ratios, which illustrates an enhanced degree of photochemical processing of diacids during summertime. The $\delta^{13}C$ values of C_4 were negatively correlated with WSOC/OC ratios in the cold seasons (autumn: 0.31, winter: 0.45), demonstrating an enrichment of $\delta^{13}C$ in C_4 with decreasing WSOC/OC ratios. Ph displayed negatively weak correlations in summer, while ωC_2 presented weakly positive and negative relations in autumn (0.2) and spring (0.29), respectively. The positive relationship between the $\delta^{13}C$ values of Pyr and WSOC/OC in autumn (0.62) suggests that an isotopic enrichment of Pyr increases with high WSOC/OC ratios, which may have resulted in the largest $\delta^{13}C$ values of Pyr in autumn. There are no correlations between C_2, tPh and C_9 with the WSOC/OC ratios in the Beijing samples. Thus, the results discussed above suggest that primary emissions in local regions significantly impact diacids and related compounds in Beijing.

4 Summary and conclusions

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

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

On the basis of the weak correlations of C_2/Tot and WSOC/OC with seasonal $\delta^{13}C$ values of major species, the results of the principal component analysis, and the comparison of $\delta^{13}C$ values in Beijing with those in urban and remote marine aerosols, we can conclude that photochemical production of dicarboxylic acids and related compounds in the Beijing aerosols slightly increased in summer. But the abundance of diacids and related polar acids in fine aerosols in Beijing are mainly associated with anthropogenic primary emissions such as biomass burning, fossil fuel combustion and plastic burning. Further study is needed to interpret the detailed mechanisms of the enrichment of the $\delta^{13}C$ values of C_3 and C_4 diacids and to better evaluate the impact of micro-biological degradation along with contact-induced chemical changes on the aerosol chemistry in Beijing.

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Table 1. Seasonal concentrations (ng m^{-3}) of dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in 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
Pimeric, 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
Dodecanedioc, 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, ωC_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, ωC_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, ωC_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, ωC_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, ωC_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, ωC_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, ωC_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

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

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>tPh>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_2>Ph>iPh>tPh	0.41		Wang et al. [2006a]
Hong Kong, China	Feb 2004	$PM_{2.5}$	114–812 (771)	C_2>Ph>iPh>tPh	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>tPh	(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			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)	tPh>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>tPh	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>tPh	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_4>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.

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

	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	0.69±0.14	0.59±0.11	0.88±0.09	0.99±0.1
C_6/C_9	0.53±0.24	0.34±0.13	0.55±0.21	0.59±0.28
Ph/C_9	0.82±0.39	1.4±0.69	0.92±0.33	1.33±0.39
Ph/C_6	1.7±0.78	4.1±0.78	1.8±0.85	2.5±0.76
M/F	1.7±0.81	2.0±0.66	2.0±0.67	1.4±0.49
hC_4/C_4	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	0.7±0.27	0.49±0.11	0.56±0.07	0.58±0.1

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

	Sampling year	
Species	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%

Table 5. Stable carbon isotopic compositions ($\delta^{13}C$, ‰) of major compounds in $PM_{2.5}$ in Beijing.

Compounds	Autumn			Winter			Spring			Summer		
	Min	Max	Mean±SD	Min	Max	Mean±SD	Min	Max	Mean±SD	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

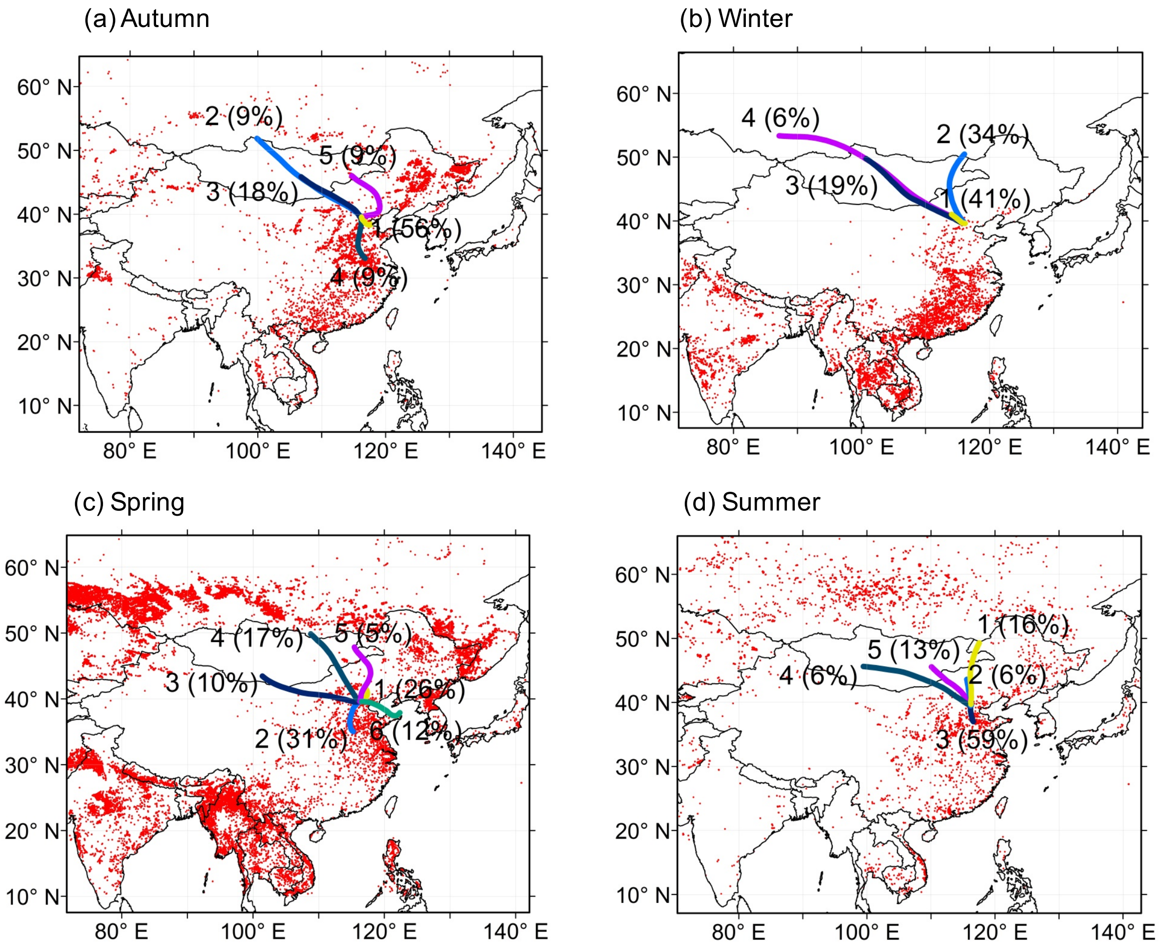

Figure 1. Fire spots with typical 5-day air mass backward trajectories (mean clusters) arriving at Beijing for each sampling season. The fire spot data were obtained from the MODIS fire spot website (https://firms.modaps.eosdis.nasa.gov/download/request.php). The air mass trajectories were drawn using the data obtained by HYSPLIT4 model from the NOAA ARL website (http://ready.arl.noaa.gov/HYSPLIT.php). The numbers in each panel imply the percentages of hourly trajectories in the sampling season with air mass origins. The arrival height of the air mass backward trajectories was 500 m above sea level.

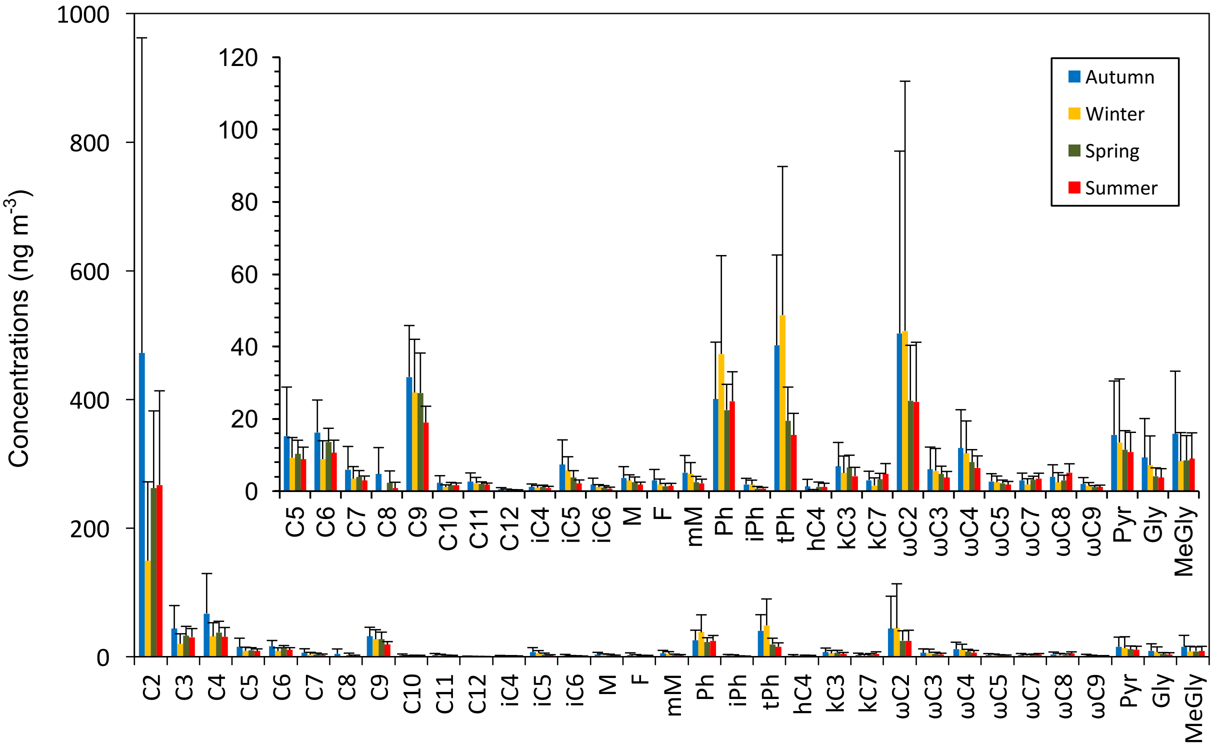

Figure 2. Molecular distributions of dicarboxylic acids and related compounds in the $PM_{2.5}$ samples collected in Beijing from 30 September 2013 to 12 July 2014.

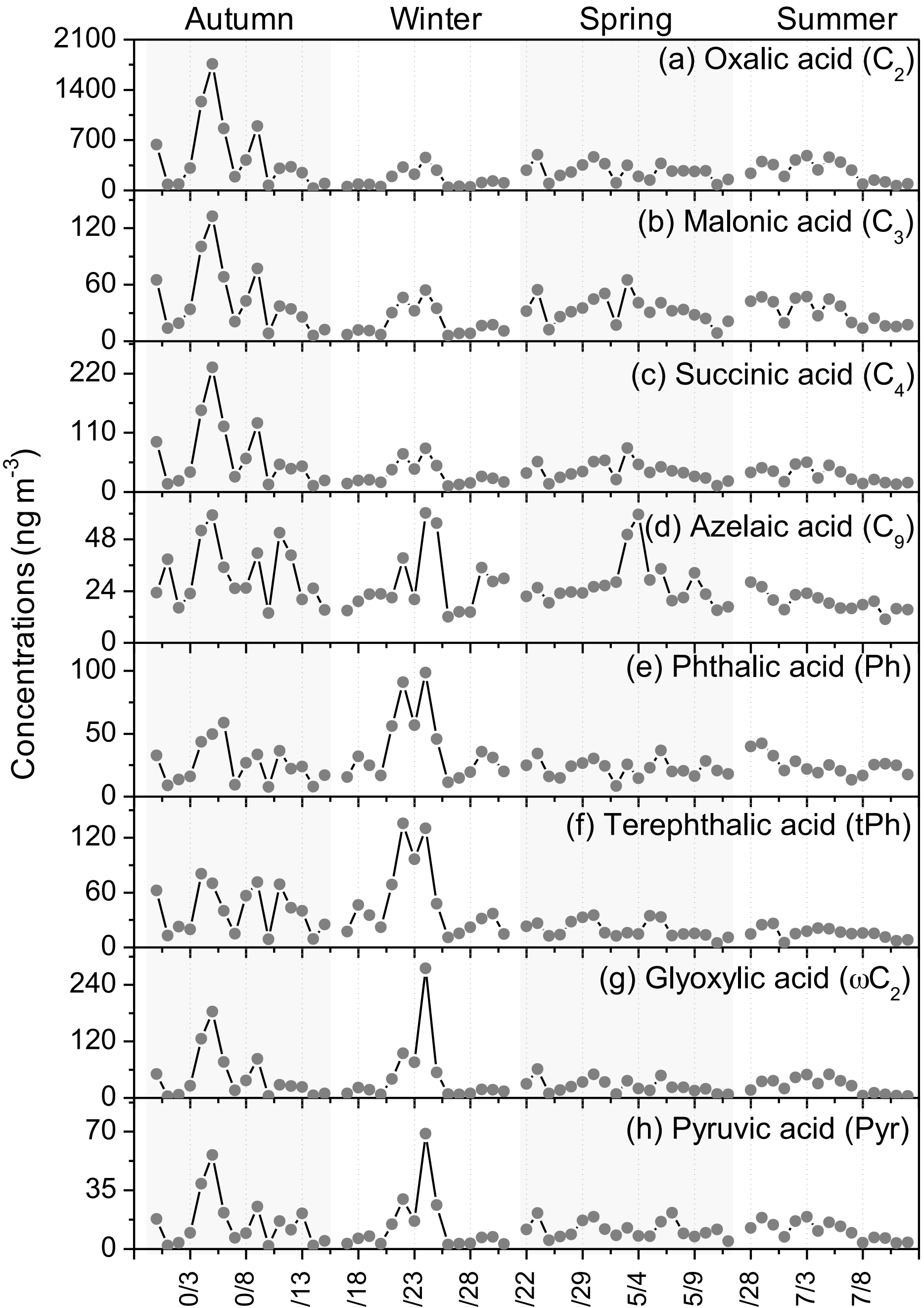

Figure 3. Daily variations in the concentrations of selected organic acids in the $PM_{2.5}$ aerosols in Beijing.

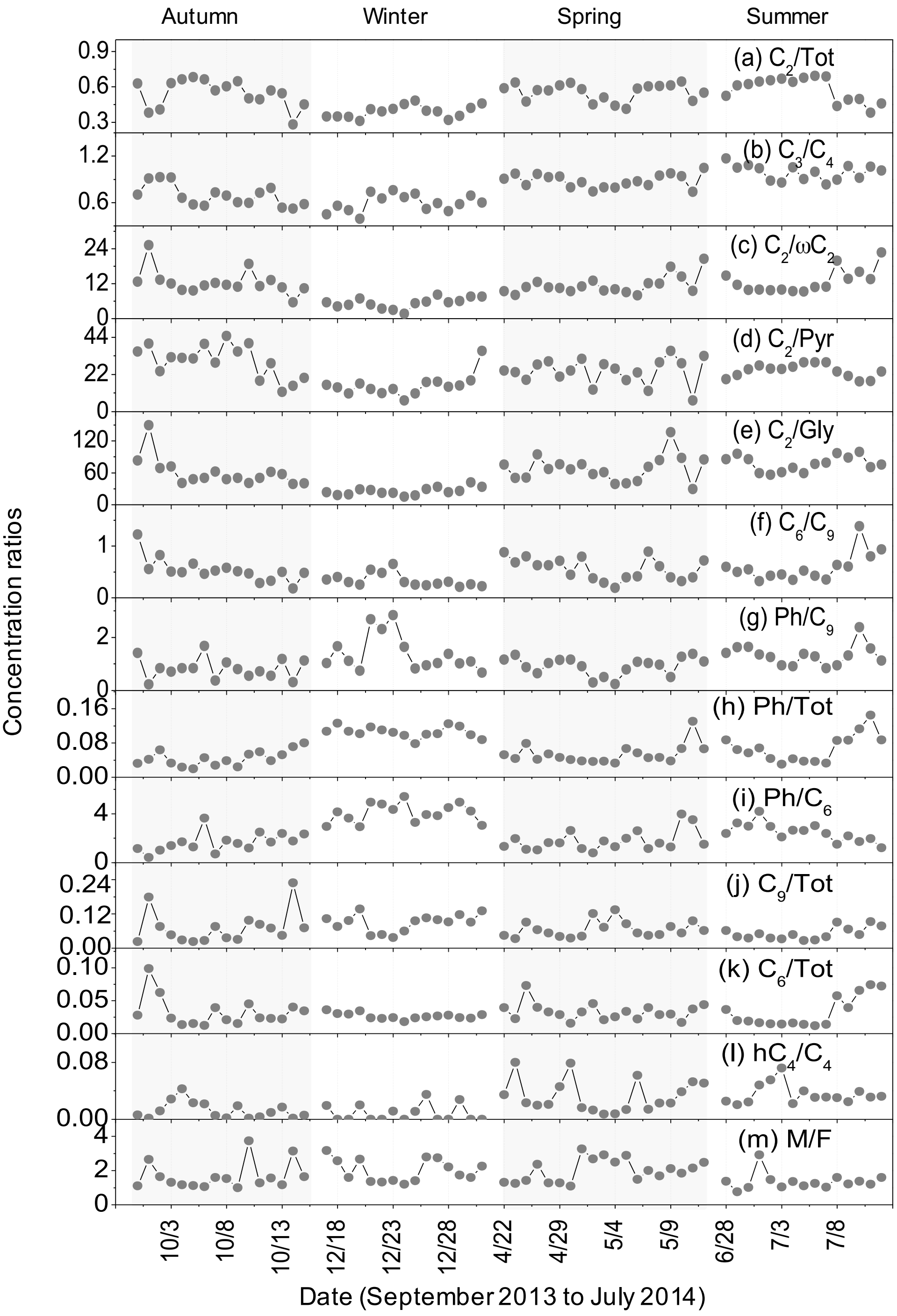

Figure 4. Seasonal variations in the concentration ratios of (a) C_2/Tot, (b) C_3/C_4, (C) $C_2/\omega C_2$, (d) C_2/Pyr, (e) C_2/Gly, (f) C_6/C_9, (g) Ph/C_9, (h) Ph/Tot, (i) Ph/C_6, (j) C_9/Tot, (k) C_6/Tot, (l) hC_4/C_4, and (m) M/F in the Beijing aerosols.

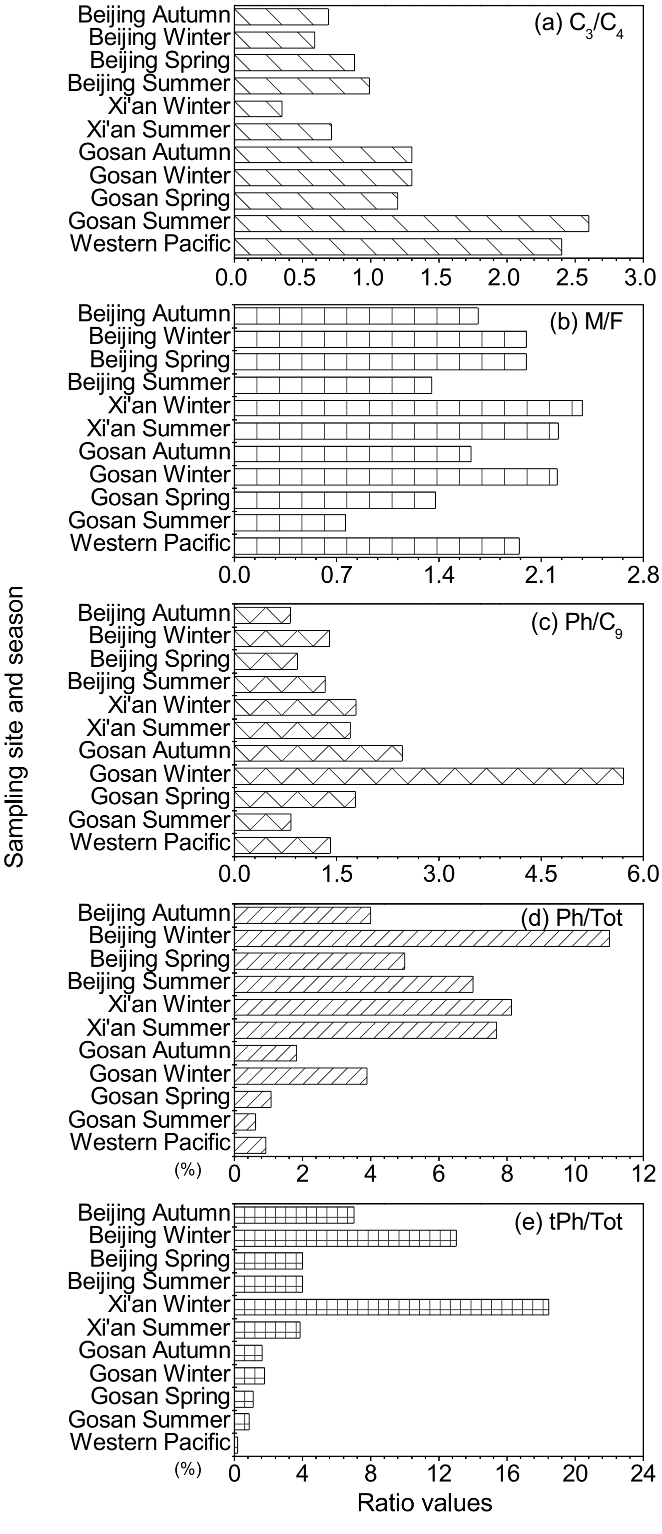

Figure 5. Mean mass ratios of (a) C_3/C_4, (b) M/F, (c) Ph/C_9, (d) Ph/Tot, and (e) tPh/Tot from this study compared with those in Xi'an (Wang et al., 2012), Gosan, Jeju Island (Kundu et al., 2010a) and the western Pacific (Wang et al., 2006b) aerosols.

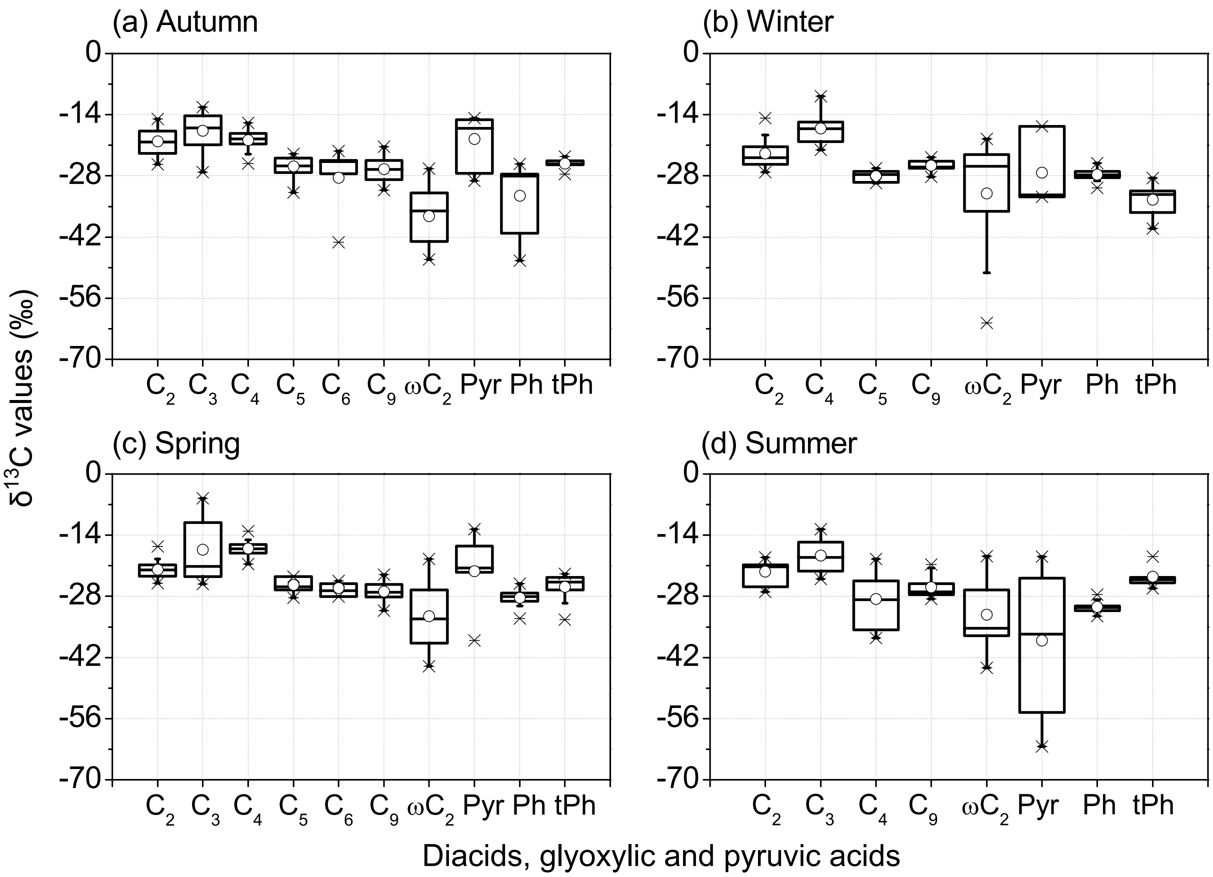

Figure 6. Box plot of the $\delta^{13}C$ values of diacids, glyoxylic and pyruvic acids. The small circles represent the average $\delta^{13}C$ values.

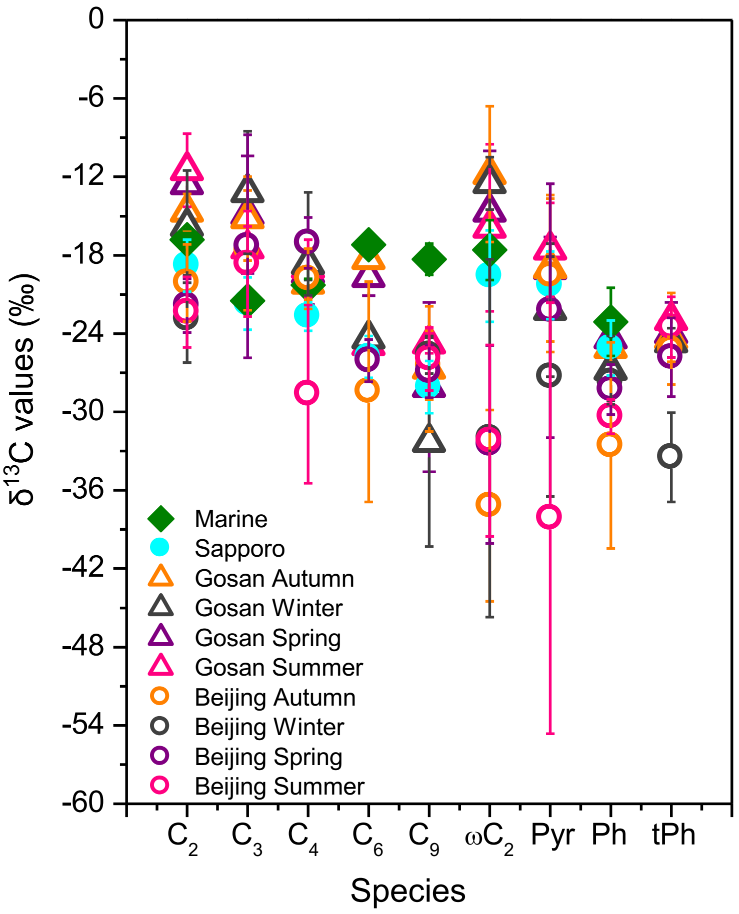

Figure 7. Seasonal mean $\delta^{13}C$ values of selected diacids and related compounds detected in $PM_{2.5}$ in Beijing. Data from Saporro (Aggarwal and Kawamura, 2008), Gosan, Jeju Island (Zhang et al., 2016) and marine (Kawamura and Watanabe, 2004;Wang and Kawamura, 2006) aerosols are also plotted. The bar represents the standard variation (±SD) in the $\delta^{13}C$ values.

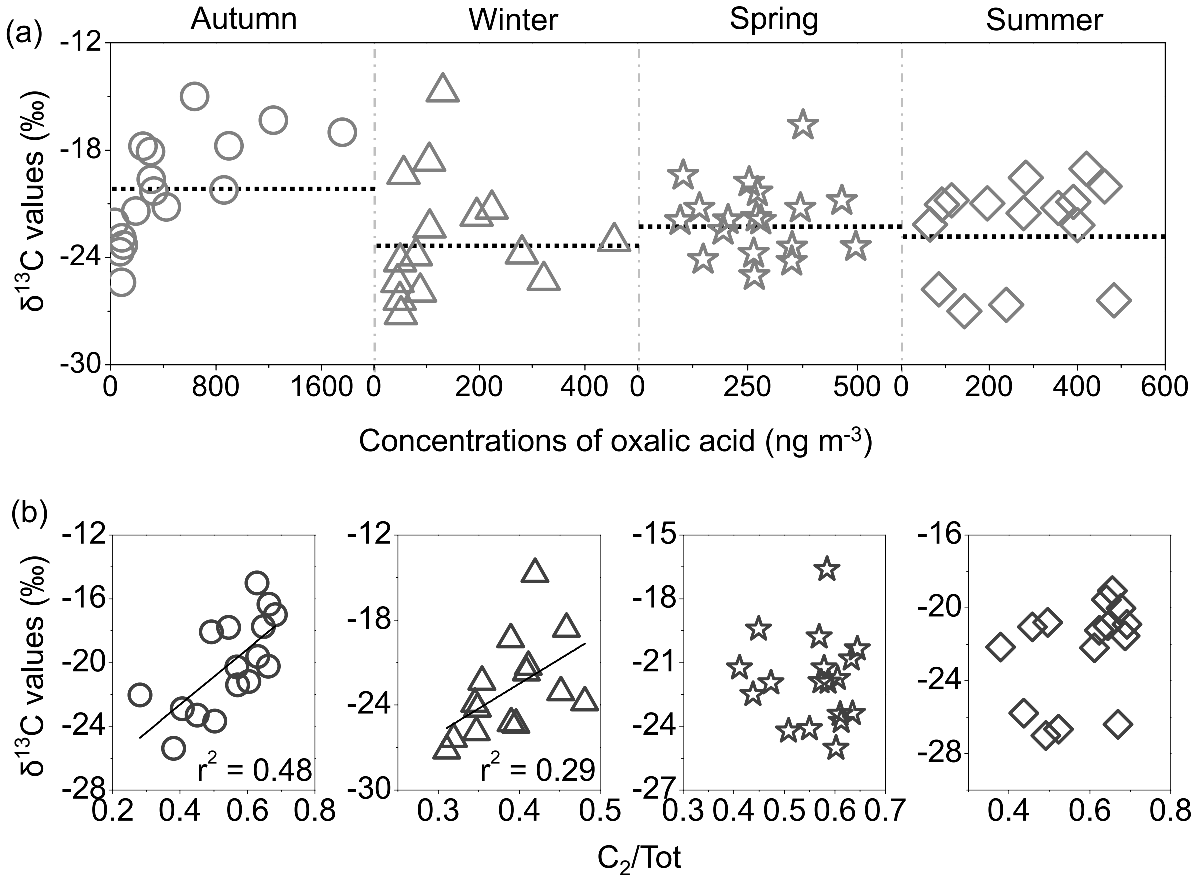

Figure 8. (a) Seasonal variations in the stable carbon isotope ratios ($\delta^{13}C$) of C_2, (b) correlations between $\delta^{13}C$ values of C_2 and relative abundances of oxalic acid to total diacids (C_2/Tot) in $PM_{2.5}$ in Beijing. The black dotted lines represent the average $\delta^{13}C$ values.

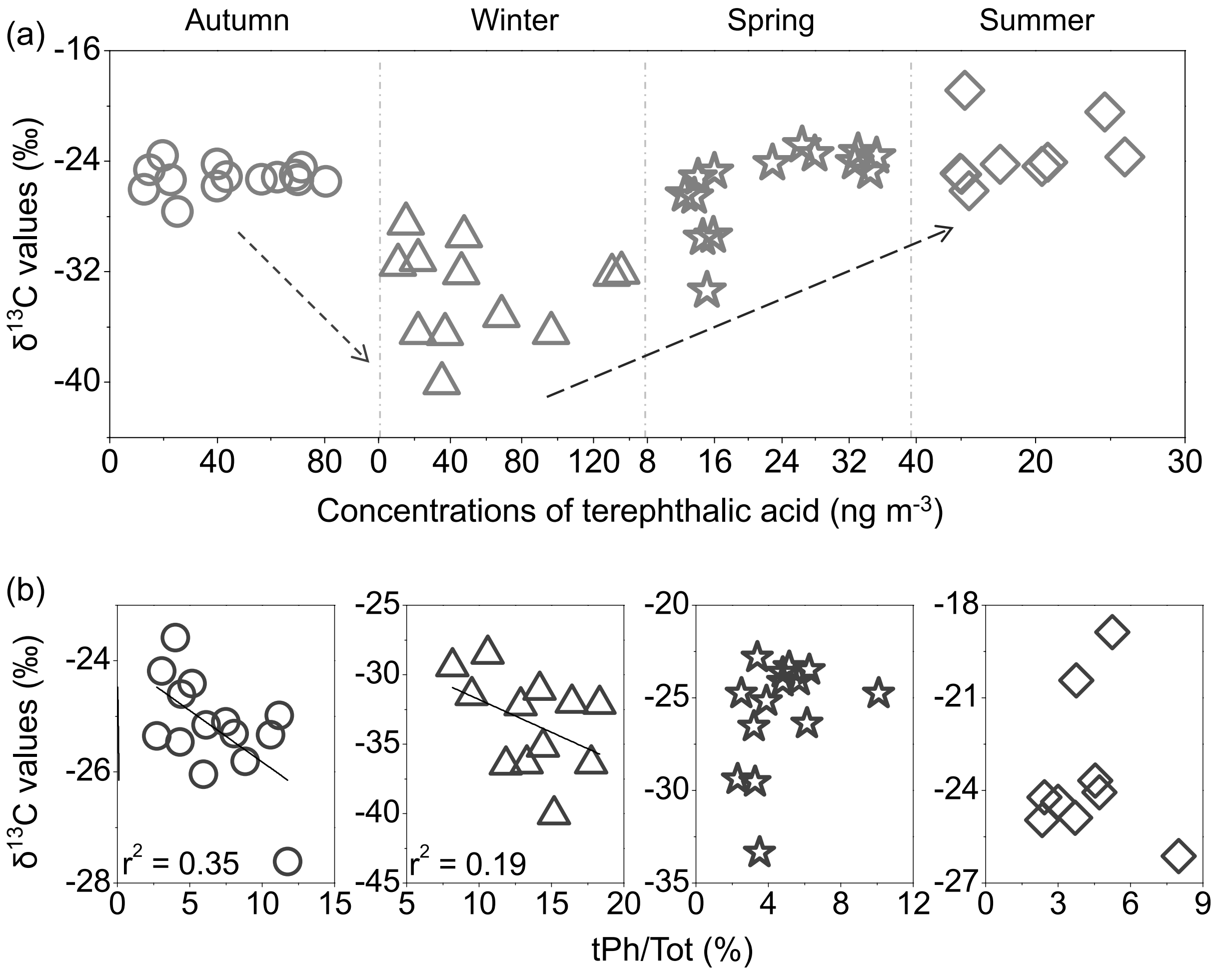

Figure 9. (a) Seasonal variations in stable carbon isotope ratios ($\delta^{13}C$) of tPh, (b) correlations between the $\delta^{13}C$ values of tPh and relative abundances of terephthalic acid to total diacids (tPh/Tot) in $PM_{2.5}$ in Beijing.

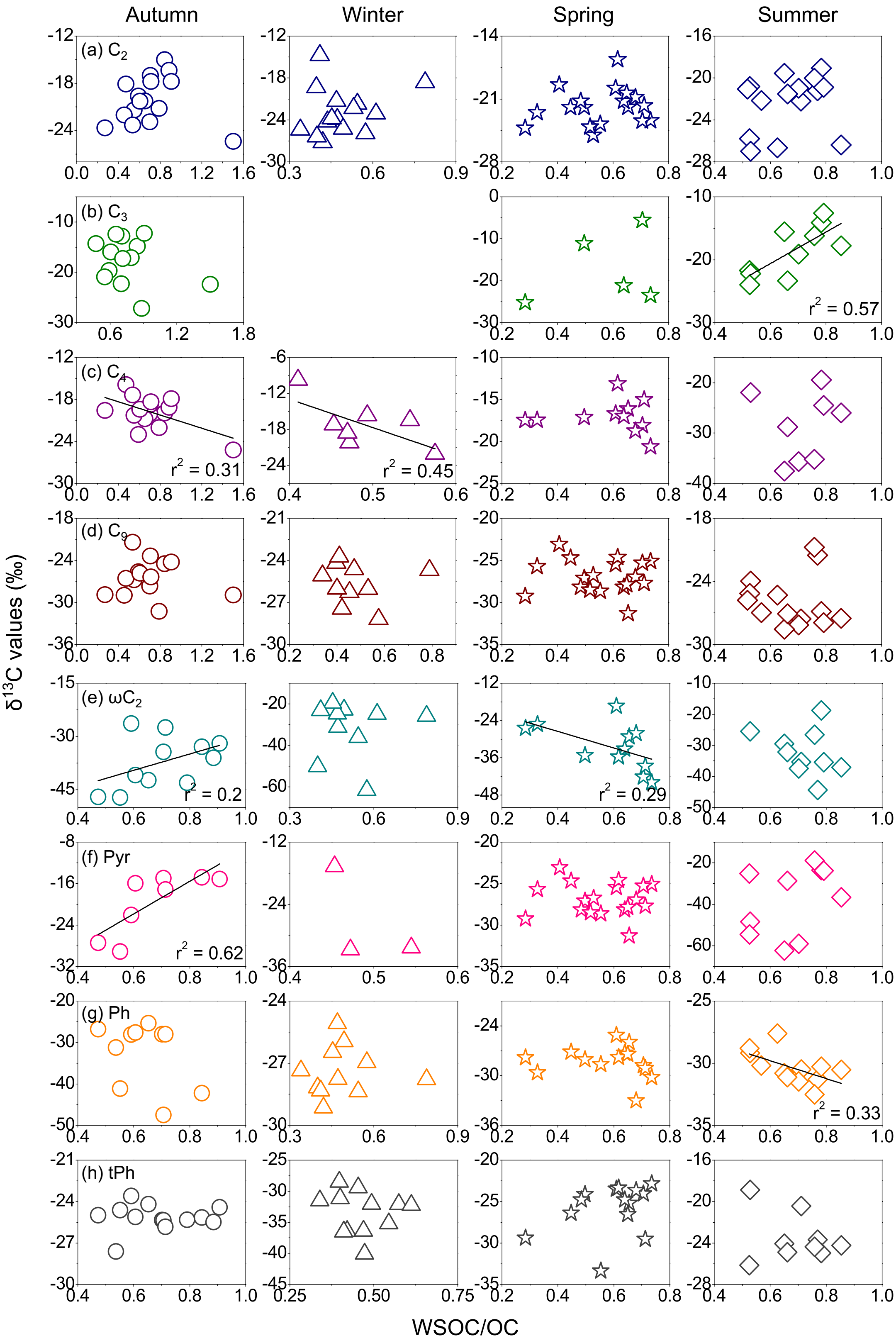

Figure 10. Correlations between compound-specific stable carbon isotope ratios of selected diacids and oxoacids and WSOC/OC ratios in $PM_{2.5}$ from urban Beijing.