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**Journal of Geophysical Research: Atmospheres****RESEARCH ARTICLE**

10.1002/2015JD024081

**Key Points:**

- $\delta^{13}\text{C}$  of diacids and related compounds was measured for East Asian aerosols
- $\delta^{13}\text{C}$  results show that oxalic acid is mainly from aqueous phase oxidation
- Organic aerosols are intensively photochemically aged in East Asia

**Supporting Information:**

- Supporting Information S1

**Correspondence to:**

Y.-L. Zhang, and K. Kawamura,  
kkawamura@isc.chubu.ac.jp  
dryanlinzhang@gmail.com

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## **Stable carbon isotopic compositions of low-molecular-weight dicarboxylic acids, oxocarboxylic acids, $\alpha$ -dicarbonyls, and fatty acids: Implications for atmospheric processing of organic aerosols**

**Yan-Lin Zhang<sup>1,2</sup>, Kimitaka Kawamura<sup>1,3</sup>, Fang Cao<sup>2</sup>, and Meehye Lee<sup>4</sup>**

<sup>1</sup>Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan, <sup>2</sup>Yale-NUIST Center on Atmospheric Environment, Nanjing University of Information Science and Technology, Nanjing, China, <sup>3</sup>Now at Chubu Institute for Advanced Studies, Chubu University, Kasugai, Japan, <sup>4</sup>Department of Earth and Environmental Sciences, Korea University, Seoul, South Korea

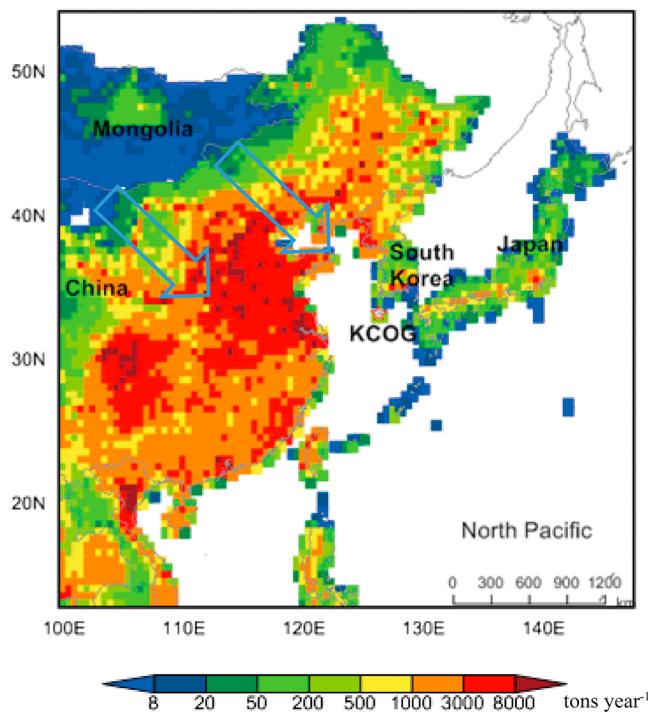
**Abstract** Stable carbon isotopic compositions ( $\delta^{13}\text{C}$ ) were measured for 23 individual organic species including 9 dicarboxylic acids, 7 oxocarboxylic acids, 1 tricarboxylic acid, 2  $\alpha$ -dicarbonyls, and 4 fatty acids in the aerosols from Gosan background site in East Asia.  $\delta^{13}\text{C}$  values of particle phase glyoxal and methylglyoxal are significantly larger than those previously reported for isoprene and other precursors. The values are consistently less negative in oxalic acid ( $\text{C}_2$ , average  $-14.1\text{\textperthousand}$ ), glyoxylic acid ( $-13.8\text{\textperthousand}$ ), pyruvic acid ( $-19.4\text{\textperthousand}$ ), glyoxal ( $-13.5\text{\textperthousand}$ ), and methylglyoxal ( $-18.6\text{\textperthousand}$ ) compared to other organic species (e.g., palmitic acid,  $-26.3\text{\textperthousand}$ ), which can be explained by the kinetic isotope effects during atmospheric oxidation of pre-aged precursors (e.g., isoprene) and the subsequent gas-particle partitioning after the evaporation of clouds or wet aerosols. The  $\delta^{13}\text{C}$  values of  $\text{C}_2$  is positively correlated with  $\text{C}_2$  to organic carbon ratio, indicating that photochemical production of  $\text{C}_2$  is more pronounced than its degradation during long-range atmospheric transport. The isotopic results also suggest that aqueous phase oxidation of glyoxal and methylglyoxal is a major formation process of oxalic acid via the intermediates such as glyoxylic acid and pyruvic acid. This study provides evidence that organic aerosols are intensively photochemically aged in the western North Pacific rim.

### **1. Introduction**

Organic aerosols typically contribute 20–50% of the total atmospheric aerosol mass, in which 40–80% of the organic aerosols are water soluble [Timonen et al., 2010; Zhang et al., 2007]. Dicarboxylic acids and their related polar compounds have been found as one of the most abundant water-soluble organic compound classes in aerosols from the urban [Ho et al., 2007; van Pinxteren et al., 2014], continental background [Limbeck and Puxbaum, 1999], remote marine [Wang and Kawamura, 2006], and Arctic [Kawamura et al., 1996] environments. Due to their water-soluble and hygroscopic properties, dicarboxylic acids play important roles in atmospheric chemistry via atmospheric processing (e.g., secondary aerosol formation) and in Earth's climate by enhancing the ability of organic aerosols to act as cloud condensation nuclei [Kawamura and Bikkina, 2016; Kumar et al., 2003; Peng et al., 2001].

Previous studies suggest that dicarboxylic acids and related compounds can be emitted from primary sources including fossil fuel combustion [Kawamura and Kaplan, 1987] and biomass burning [Narukawa et al., 1999]. They can also be formed by secondary photochemical oxidation of unsaturated fatty acids [Kawamura et al., 1996] and cyclic alkenes [Hatakeyama et al., 1987] and thus serve as tracers for secondary organic aerosols. Cloud and other field measurements as well as modeling studies show that aqueous phase oxidation of less oxygenated organics such as glyoxal (Gly), methylglyoxal (MeGly), and pyruvic acid (Pyr) in wet aerosols or clouds is more important as a source of small dicarboxylic acids [Carlton et al., 2007; Carlton et al., 2006; Lim et al., 2005; Lim et al., 2013; Yu et al., 2005]. Due to the large variety of primary and secondary sources of dicarboxylic acids and related compounds, it is therefore often difficult to evaluate the contributions of the different sources and formation pathways in field studies.

Compound-specific stable carbon isotope analysis is a powerful tool to provide important information of the sources and atmospheric processing of organic aerosols. Many studies have revealed that the  $\delta^{13}\text{C}$  values of longer-chain dicarboxylic acids are often lower than those of shorter-chain dicarboxylic acids [Wang and Kawamura, 2006]. For example, it has been reported that oxalic acid is more enriched in  $^{13}\text{C}$  than malonic,



**Figure 1.** Map of East Asia with emission inventories estimated for anthropogenic total carbonaceous aerosols (or total carbon) as sum of black carbon and organic carbon in  $\text{t yr}^{-1}$  per  $0.5 \times 0.5^\circ$  grid for East Asia in 2006 (data obtained from Zhang et al. [2009]). The sampling site is marked as a red star (Korea Climate Observatory at Gosan, KCOG). The blue arrows indicate the prevailing pathway of East China continental outflow.

America [Carmichael et al., 2009; de Gouw et al., 2004]. In this study, we report stable carbon isotopic compositions of a homologous series of low-molecular-weight dicarboxylic acids, oxocarboxylic acids,  $\alpha$ -dicarbonyls, and fatty acids in aerosol samples from Gosan, Jeju Island, Korea, during April 2013 to April 2014. To the best of our knowledge, the data set presents one of the most comprehensive studies, including stable carbon isotope ratios of 23 individual dicarboxylic acids and related compounds. These results could provide important information of the sources and atmospheric processing of organic aerosols in East Asia.

## 2. Experimental

### 2.1. Sample Collection

Total suspended particles (TSP) in the atmosphere were collected at the Korea Climate Observatory at Gosan (KCOG), a background supersite ( $33.17^\circ\text{N}, 126.10^\circ\text{E}$ , see Figure 1) in East Asia approximately every 2 weeks for 10–14 days sampling durations throughout 1 year from April 2013 to April 2014. Detailed information of the sampling site has been described elsewhere [Jung and Kawamura, 2011]. The Gosan site is located on the western edge of Jeju Island facing the Asian continent (~100 km south of the Korean Peninsula, ~500 km east of China, and ~200 km west of Kyushu Island, Japan), and the sampling site is far away from local residential areas of the island. TSP samples ( $n = 21$ ) were collected on preheated quartz fiber filters using a high-volume air sampler (Kimoto AS-810,  $\sim 65 \text{ m}^3 \text{ h}^{-1}$ ) installed on the roof of a trailer house (~3 m above the ground). After the sampling, filters were put in a precombusted ( $450^\circ\text{C}$  for 6 h in the oven with ambient atmosphere) glass jar (150 mL) with a Teflon-lined screw cap to avoid potential contamination and stored in a dark freezer room at  $-20^\circ\text{C}$  until analysis. Field blank filters were collected every month.

### 2.2. Chemical Analysis

#### 2.2.1. Mass Concentrations of Dicarboxylic Acids, Oxoacids, $\alpha$ -Dicarbonyls, and Fatty Acids

Before  $^{13}\text{C}$  measurement, mass concentrations of low-molecular-weight dicarboxylic acids (or diacids), oxocarboxylic acids (or oxoacids),  $\alpha$ -dicarbonyls, and fatty acids were determined as described elsewhere

succinic, and glyoxylic acids. This difference suggests either that oxalic acid is formed from the oxidation of  $^{13}\text{C}$ -enriched precursors or that it is photochemically processed. During this chemical aging, the lighter isotope accumulates in products, while the remaining reactant (i.e., oxalic acid) is enriched with  $^{13}\text{C}$  [Aggarwal and Kawamura, 2008; Mkoma et al., 2014; Pavuluri and Kawamura, 2012]. In addition to dicarboxylic acids, a simultaneous measurement of  $\delta^{13}\text{C}$  for oxocarboxylic acids,  $\alpha$ -dicarbonyls, and fatty acids would contribute to better understand the formation of dicarboxylic acids and related compounds.

East Asia has become a major source region of anthropogenic aerosols with its rapid economic growth and energy consumption [Bond et al., 2004; Zhang et al., 2009]. Continental outflow of polluted organic aerosols from East Asia can affect not only the local/regional air quality [Huang et al., 2014; Zhang et al., 2015] but also the free troposphere via long-range transport across the Pacific Ocean to North

**Table 1.** Compound-Specific Stable Carbon Isotope Ratios ( $\delta^{13}\text{C}$ , ‰) of Low Molecular Weight Dicarboxylic Acids and Related Polar Compounds in Aerosols From Gosan Site<sup>a</sup>

Compounds	Spring		Summer		Autumn		Winter	
	Range	Mean (SD)	Range	Mean (SD)	Range	Mean (SD)	Range	Mean (SD)
Oxalic acid, C <sub>2</sub>	-15.0 to -10.6	-12.6 (1.4)	-14.1 to -7.5	-11.5 (2.8)	-16.7 to -13.2	-14.7 (1.4)	-20.5 to -10.1	-15.8 (4.3)
Malonic acid, C <sub>3</sub>	-19.9 to -7.2	-14.9 (4.5)	-19 to -16	-17.5 (1.7)	-18.7 to -10.2	-15.2 (3.2)	-19.7 to -8.7	-13.2 (4.7)
Succinic acid, C <sub>4</sub>	-24.2 to -17.0	-19.4 (2.4)	-21.1 to -16.9	-19 (2.2)	-22.1 to -19	-20.2 (1.2)	-19.8 to -17.2	-18.7 (1.2)
Glutaric acid, C <sub>5</sub>	-28.8 to -21.9	-23.8 (2.3)	-40.9 to -23.3	-32.1 (12.5)	-29.7	-29.7	-28.2 to -14.2	-21.2 (10.0)
Adipic acid, C <sub>6</sub>	-20.7 to -18.7	-19.7 (1.4)	-24.9	-24.9	-18.3	-18.3	-24.4	-24.4
4-Ketopimelic acid, kC <sub>7</sub>	-24.0 to -18.9	-21.4 (3.6)	-20.6	-20.6	-21.5	-21.5	NA	NA
Terephthalic acid, tPh	-28.0 to -21.6	-24 (2.4)	-23.0	-23.0	-28.9 to -20.6	-24.4 (3.5)	-26 to -23.7	-24.7 (1.1)
Phthalic acid, Ph	-27.3 to -23	-24.4 (1.7)	NA	NA	-26.5 to -21.4	-25.1 (2.1)	-30.5 to -24.9	-26.8 (2.6)
Azelaic acid, C <sub>9</sub>	-36.8 to -22.5	-28.1 (6.5)	-25.4 to -24.1	-24.8 (0.7)	-31.9 to -21	-26.7 (4.8)	-37.9 to -26.6	-32.3 (8)
Glyoxylic acid, $\omega\text{C}_2$	-22.5 to -8.7	-14.7 (4.7)	-24.2 to -9.8	-15.9 (6.4)	-16.7 to -3.8	-11.8 (5.2)	-14.5 to -10.1	-12.5 (2)
Pyruvic acid, Pyr	-22.2 to -15.7	-19.1 (2.5)	-20.7 to -12.3	-17.6 (3.6)	-25.2 to -12.8	-19 (5.6)	-25.6 to -14.7	-22.2 (5.1)
3-Oxopropanoic acid, $\omega\text{C}_3$	-23.9 to -7.5	-18.0 (5.1)	-13.3 to -13.3	-13.3 (0)	-28.5 to -9	-17.4 (9.9)	-33.2 to -6.3	-18.5 (11.1)
4-Oxobutanoic acid, $\omega\text{C}_4$	-20.1 to -14.2	-17.9 (1.9)	-23.7 to -23.7	-23.7 (0)	-37.1 to -9.3	-24.2 (11.9)	-20.6 to -16.8	-18.8 (1.6)
7-Oxoheptanoic, $\omega\text{C}_7$	-23.9 to -15.4	-21.3 (2.7)	-25.2 to -19.2	-22.6 (2.6)	-26.5 to -18.4	-22.9 (3.3)	-32.6 to -21.3	-25.1 (5.1)
8-Oxoctanoic acid, $\omega\text{C}_8$	-32.4 to -20.6	-25.7 (3.9)	-25.8 to -17.6	-21.8 (3.7)	-26.1 to -20.4	-22.3 (2.6)	-24.3 to -20.4	-22.1 (2.0)
9-Oxononoic acid, $\omega\text{C}_9$	-26.6 to -18.5	-23.4 (2.9)	-22.3 to -16.9	-19.9 (2.3)	-26 to -21.1	-23.7 (2)	-25.8 to -21.8	-23.5 (1.7)
Citric acid, Cit	-33.0 to -23.4	-27.8 (4.2)	NA	NA	NA	NA	NA	NA
Glyoxal, Gly	-18.4 to -5.0	-10.6 (5.2)	-22.8 to -16.8	-20.8 (3.4)	-25.9 to -10.9	-16.6 (6.5)	-15.9 to -8.1	-11.2 (3.3)
Methylglyoxal, MeGly	-22 to -14.7	-18.1 (2.5)	-23.3 to -11.8	-17.7 (5.7)	-18.5 to -16.5	-17.7 (0.8)	-17.8 to -13.7	-16.2 (1.9)
Myristic acid, C <sub>14:0</sub>	-27.6 to -23.9	-26.3 (1.6)	NA	NA	-29.6 to -26.7	-27.6 (1.3)	-32.1 to -24	-27.7 (3.3)
Palmitic acid, C <sub>16:0</sub>	-26.7 to -24.4	-25.8 (1)	-27.2 to -26.3	-26.9 (0.5)	-28.8 to -23.7	-26.3 (1.8)	-26.9 to -25.5	-26.2 (1.0)
Stearic acid, C <sub>18:0</sub>	-28.3 to -27.9	-28.1 (0.3)	-26.0	-26.0	-30.1 to -26.4	-27.8 (1.4)	-28.0	-28.0
Oleic acid, C <sub>18:1</sub>	-27.9 to -27.8	-27.9 (0.1)	-26.2 to -25.5	-26 (0.5)	-27.9 to -25.6	-26.6 (0.9)	-28.1	-28.1

<sup>a</sup>NA: not available.

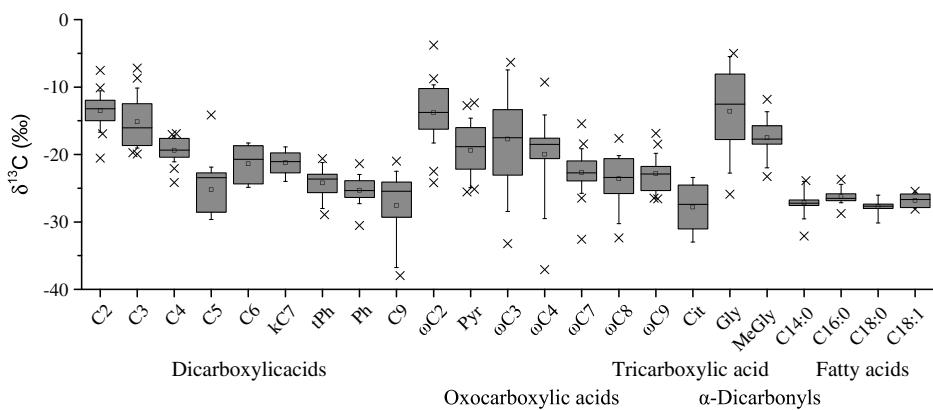
[Ho et al., 2010; Kawamura and Ikushima, 1993]. Briefly, a filter aliquot of 1.54 to 3.08 cm<sup>2</sup> was extracted with organic free ultrapure water (10 mL × 3) in a glass vial for 10 min. The extracts were passed through a Pasteur pipette packed with quartz wool to remove insoluble particles and filter debris. The pH of the extracts was then adjusted to 8.5–9.0 with 0.1 M KOH solution, concentrated to near dryness with a rotary evaporator under vacuum, and then reacted with 14% BF<sub>3</sub>/n-butanol to derivatize carboxyl group to dibutyl ester and oxo groups to dibutoxy acetals.

The derivatives were extracted with n-hexane, concentrated to near dryness, dissolved in n-hexane, and finally determined using a gas chromatograph (GC) with an aflame ionization detector. Identifications of the compounds were performed by GC retention times and GC/mass spectrometry (MS) analyses. Small peaks of oxalic, malonic, and glyoxylic acids were found in the field blank filters, but they were <5% of the real samples. The concentrations reported here are all corrected for the field blanks. Their concentrations are compiled in Table S1 (see supporting information).

Concentrations of organic carbon (OC) were measured by thermal-optical transmittance method with OC/elemental carbon Carbon Aerosol Analyzer (Sunset Laboratory Inc., USA) following the NIOSH (The National Institute for Occupational Safety and Health) protocol [Birch and Cary, 1996].

### 2.2.2. Stable Carbon Compositions of Diacids, Oxoacids, $\alpha$ -Dicarbonyls, and Fatty Acids

Stable carbon isotopic compositions ( $\delta^{13}\text{C}$ ) of low-molecular-weight dicarboxylic acids, related polar compounds, and fatty acids were measured using the method developed by [Kawamura and Watanabe, 2004]. Briefly, 2  $\mu\text{L}$  of internal standard (*n*-C<sub>13</sub> alkane, -27.24‰) was spiked to an aliquot of the derivative samples.  $\delta^{13}\text{C}$  values of the derivatives relative to Pee Dee Belemnite were determined by GC-combustion-isotope ratio mass spectrometry (Thermo Delta V). The  $\delta^{13}\text{C}$  values were then calculated for free organic acids using an isotopic mass balance equation based on the measured  $\delta^{13}\text{C}$  values of derivatives and the derivatizing agent (BF<sub>3</sub>/n-butanol). Prior to actual sample analysis, we confirmed that  $\delta^{13}\text{C}$  values of the working standards (a mixture of normal C<sub>16</sub>–C<sub>30</sub> alkanes with 0.55–2.83 ng/ $\mu\text{L}$ ) were equivalent to the theoretical values within an analytical error of <0.2‰. The difference in  $\delta^{13}\text{C}$  values of major compounds (i.e., C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>9</sub>, Ph,  $\omega\text{C}_2$ , Gly, and MeGly, see Table 1) for replicate analyses was generally <1‰ though the analytical accuracy was 2% for other species.



**Figure 2.** Box-and-whisker plot of stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) of nine dicarboxylic acids ( $\text{C}_2$ ,  $\text{C}_3$ ,  $\text{C}_4$ ,  $\text{C}_5$ ,  $\text{C}_6$ ,  $\text{C}_9$ ,  $\text{kC}_7$ ,  $\text{tPh}$ , and  $\text{Ph}$ ), seven oxocarboxylic acids ( $\omega\text{C}_2$ ,  $\text{Pyr}$ ,  $\omega\text{C}_3$ ,  $\omega\text{C}_4$ ,  $\omega\text{C}_7$ ,  $\omega\text{C}_8$ , and  $\omega\text{C}_9$ ), one tricarboxylic acid ( $\text{Cit}$ ), two  $\alpha$ -dicarbonyls ( $\text{Gly}$  and  $\text{MeGly}$ ), and four fatty acids ( $\text{C}_{14:0}$ ,  $\text{C}_{16:0}$ ,  $\text{C}_{18:0}$ , and  $\text{C}_{18:1}$ ) in aerosols ( $n = 21$ ) from April 2013 to April 2014. Each box shows the median (black line), mean (square), the interquartile range (box), and the 10th percentile and ninetieth percentile (the whiskers). The crosses show the outliers.

### 3. Results and Discussion

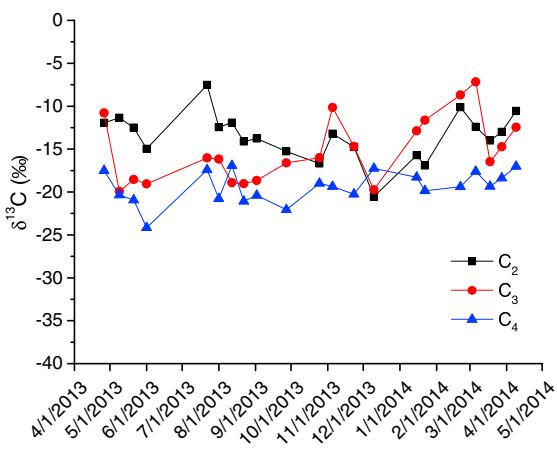
#### 3.1. Summary of $\delta^{13}\text{C}$ Results

The statistical distributions of  $\delta^{13}\text{C}$  values of nine dicarboxylic acids (i.e., diacids including  $\text{C}_2$ ,  $\text{C}_3$ ,  $\text{C}_4$ ,  $\text{C}_5$ ,  $\text{C}_6$ ,  $\text{C}_9$ ,  $\text{kC}_7$ ,  $\text{tPh}$ , and  $\text{Ph}$ ), seven oxocarboxylic acids (i.e., oxoacids including  $\omega\text{C}_2$ ,  $\text{Pyr}$ ,  $\omega\text{C}_3$ ,  $\omega\text{C}_4$ ,  $\omega\text{C}_7$ ,  $\omega\text{C}_8$ , and  $\omega\text{C}_9$ ), two  $\alpha$ -dicarbonyls ( $\text{Gly}$  and  $\text{MeGly}$ ), one tricarboxylic acid ( $\text{Cit}$ ), and four fatty acids ( $\text{C}_{14:0}$ ,  $\text{C}_{16:0}$ ,  $\text{C}_{18:0}$ , and  $\text{C}_{18:1}$ ) in the Gosan aerosols ( $n = 21$ ) are shown in Table 1 and Figure 2. On average, smaller chain (i.e., less than five carbon numbers) diacids, oxocarboxylic acids, tricarboxylic acid, and  $\alpha$ -dicarbonyls were more enriched in  $^{13}\text{C}$  compared to longer-chain (i.e., more than four carbon numbers) diacids, oxocarboxylic acids, and fatty acids.

#### 3.2. $\delta^{13}\text{C}$ Values of Dicarboxylic Acids

The  $\delta^{13}\text{C}$  values of the three most abundant diacids ( $\text{C}_2$ ,  $\text{C}_3$ , and  $\text{C}_4$ , see Table 1) fall within the range of  $-7.2$  to  $-24.2\text{\textperthousand}$  with a mean of  $-16.0 \pm 3.8\text{\textperthousand}$  (i.e., mean  $\pm$  standard deviation), which are larger (*t* test,  $p < 0.05$ ) than those reported in previous field studies including the urban site in Sapporo, northern Japan (mean:  $-18.8\text{\textperthousand}$  for 2005) [Aggarwal and Kawamura, 2008], a marine site from Bermuda in the North Atlantic Ocean (mean:  $-21.0\text{\textperthousand}$  for 1998) [Turekian et al., 2003], an urban site in Xi'an, northern China (mean  $-21.6\text{\textperthousand}$  for 2009) [Wang et al., 2012], a rural site in Morogoro, Tanzania (mean:  $-20.2\text{\textperthousand}$  for 2011) [Mkoma et al., 2014], and a tropical site (mean:  $-20.3\text{\textperthousand}$  for 2007) [Pavuluri et al., 2011]. However, the results are similar to or only slightly larger than those (mean:  $-16.8\text{\textperthousand}$  during 1994–1995) obtained in the remote marine aerosols from the western Pacific and Southern Ocean [Wang and Kawamura, 2006]. The relatively high  $\delta^{13}\text{C}$  values of diacids found in this work may imply that organic aerosols from Gosan site may differ in their sources and atmospheric processes, as discussed below.

In general, an increase in  $\delta^{13}\text{C}$  values is observed with a decrease in carbon numbers of dicarboxylic acids, despite their relatively large variations due to the complex controlling factors of isotope fractionation during the production and degradation of diacids.  $\text{C}_2$  (the smallest dicarboxylic acid in the aerosol phase) and  $\text{C}_9$  (the largest dicarboxylic acid detected in this study) diacids show the largest and smallest mean  $\delta^{13}\text{C}$  values, respectively. On average,  $\text{C}_2$  diacid ( $-14.1 \pm 2.6\text{\textperthousand}$ ) is most enriched in  $^{13}\text{C}$  followed by  $\text{C}_3$  ( $-14.6 \pm 3.8\text{\textperthousand}$ ) and  $\text{C}_4$  diacids ( $-19.2 \pm 1.5\text{\textperthousand}$ ) (Figure 2), indicating that shorter diacids are generally more photochemically processed. This enrichment is also found in many other ambient studies, which is likely due to the enrichment of  $^{13}\text{C}$  with increased photochemical aging/photolysis of  $\text{C}_2$  or  $\text{C}_3$  diacids, that may be dependent on the rupture rate of a carbon-carbon bond to the carboxyl carbon [Pavuluri et al., 2011; Wang and Kawamura, 2006].

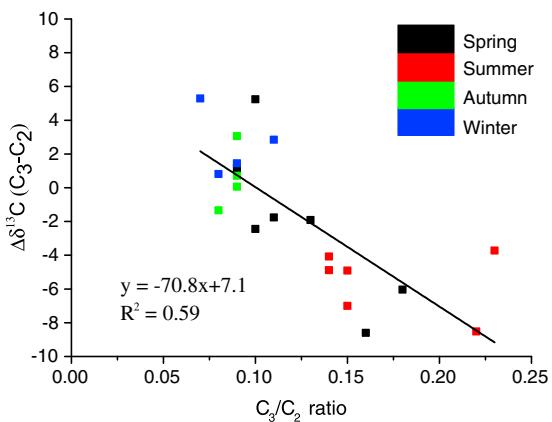


**Figure 3.** Temporal variations of stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) of oxalic ( $\text{C}_2$ ), malonic ( $\text{C}_3$ ), and succinic ( $\text{C}_4$ ) acids in aerosols from Gosan site from April 2013 to April 2014.

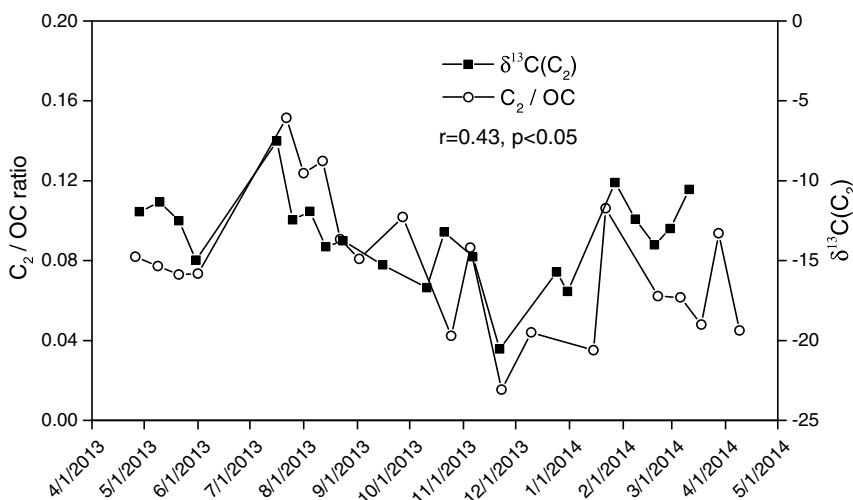
and is associated with the enhanced photochemical processing with relatively high temperature and solar radiation. Such seasonality is not found or is less pronounced for  $\text{C}_3$  and  $\text{C}_4$  diacids (Figure 3). However, it is interesting to note that the  $\delta^{13}\text{C}$  values of the  $\text{C}_3$  diacid in the cold seasons (i.e., November to March) are larger than those found in the  $\text{C}_2$  diacid, which has not yet been reported in other regions.

Figure 4 plots the differences in  $\delta^{13}\text{C}$  values of  $\text{C}_2$  and  $\text{C}_3$  ( $\Delta\delta^{13}\text{C} (\text{C}_3-\text{C}_2)$ ) as a function of the mass concentration ratio of  $\text{C}_3$  and  $\text{C}_2$  ( $\text{C}_3/\text{C}_2$ ). Interestingly,  $\Delta\delta^{13}\text{C} (\text{C}_3-\text{C}_2)$  is negatively correlated with the  $\text{C}_3/\text{C}_2$  ratio ( $R^2 = 0.59$ ,  $t$  test  $p < 0.05$ ), which indicates an enrichment of  $^{13}\text{C}$  in remaining the  $\text{C}_3$  diacid likely due to the photochemical degradation of  $\text{C}_3$  diacid and/or the depletion of  $^{13}\text{C}$  in the  $\text{C}_2$  diacid. Indeed, photochemical conditions in the East Asian atmosphere are characterized by relatively low  $\text{O}_3$  and  $\text{OH}$  concentrations during the cold seasons [Spivakovskiy *et al.*, 2000; Wang *et al.*, 2011]. Furthermore, laboratory study has demonstrated that the apparent degradation rate constants of ozonolysis and photo-assisted ozonolysis upon liquid phase  $\text{C}_3$  diacid are 2–4 orders of magnitude larger than other dicarboxylic acids (e.g.,  $\text{C}_2$ ,  $\text{C}_4$ , to  $\text{C}_9$  diacids) [Nepotchatykh and Ariya, 2002]. Hence,  $\text{C}_3$  is preferentially degraded compared to  $\text{C}_2$  and  $\text{C}_4$  during the cold seasons and  $^{12}\text{C}$  is therefore less depleted in the remaining  $\text{C}_3$  due to larger isotopic fractionation.

However, an opposite trend was observed in spring and summer when  $\text{O}_3$  and  $\text{OH}$  concentrations are very high over East China. The decomposition rates of both diacids may not be determined by ozonolysis but more likely driven by other processes when the atmospheric oxidation capacity is high. We hypothesize that production of  $\text{C}_2$  from aged precursors and photolysis of  $\text{C}_2$  in the presence of oxalate–iron complex could affect its isotopic composition. Both processes could further enhance  $^{13}\text{C}$  enrichment of  $\text{C}_2$ . Indeed, Pavuluri and Kawamura [2012] revealed a substantial increase in  $\delta^{13}\text{C}$  values in the  $\text{C}_2$  diacid during photolysis of the oxalate–iron complex, in which they proposed that  $^{12}\text{C}-^{12}\text{C}$  bonds in diacids decompose preferentially over  $^{12}\text{C}-^{13}\text{C}$  bonds during photolysis of the complex. Further laboratory studies are needed to constrain the kinetic isotopic effects of different dicarboxylic acids upon aqueous phase reactions with different photochemical conditions.



**Figure 4.** Relationships between the differences in  $\delta^{13}\text{C}$  for malonic and oxalic acids, i.e.,  $\Delta\delta^{13}\text{C} (\text{C}_3-\text{C}_2)$ , and mass concentration ratios for malonic and oxalic acids, i.e.,  $\text{C}_3/\text{C}_2$ . Different colors indicate the seasons when the samples were collected.



**Figure 5.** Temporal variations of stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) of oxalic acid ( $\text{C}_2$ ) and  $\text{C}_2$  to organic carbon ratios ( $\text{C}_2/\text{OC}$ ) in aerosols collected at Gosan site from April 2013 to April 2014.

As shown in Figure 5, the  $\delta^{13}\text{C}$  values of  $\text{C}_2$  and the  $\text{C}_2$  to OC ratio (i.e.,  $\text{C}_2/\text{OC}$ ) display similar temporal variations with a positive correlation ( $r=0.43, p < 0.05$ ). This result indicates that  $^{13}\text{C}$  enrichment of  $\text{C}_2$  is due to the production of  $\text{C}_2$  from aged precursors rather than its decomposition and is opposite to that reported in remote marine (the western Pacific and Southern Ocean) and rural continental (East Africa) aerosols [Mkoma et al., 2014; Wang and Kawamura, 2006]. In contrast to  $\text{C}_2$ , no significant correlation ( $p > 0.05$ ) is found between the relative abundances of other diacids (i.e.,  $\text{C}_3$  and  $\text{C}_4$ ) and their isotope compositions, suggesting that the difference in mechanisms of formation and decomposition of  $\text{C}_2$  and  $\text{C}_3$  (and  $\text{C}_4$ ) may affect their  $\delta^{13}\text{C}$  values, a concept that needs further laboratory studies. Nevertheless, the lesser depletion of the shorter-chain diacids suggests a different atmospheric formation process (i.e., aqueous phase oxidation) compared to the products from photochemical breakdown of longer-chain diacids or fatty acids.

$\text{C}_6$  diacid can be produced in the atmosphere by the oxidations of cyclic alkenes such as cyclohexene emitted from fossil fuel combustion or produced by photochemical oxidation of higher homologues of diacids [Kawamura et al., 1996]. An enrichment of  $^{13}\text{C}$  by 2–7‰ has been reported for organic compounds derived from biomass burning relative to the unburned  $\text{C}_3$  plant [Ballentine et al., 1998], whereas organic aerosols emitted from fossil combustion have smaller  $\delta^{13}\text{C}$  values [Widory et al., 2004]. Thus, the relatively high  $\delta^{13}\text{C}$  values of  $\text{C}_6$  diacid ranging from  $-24.9$  to  $-18.3\text{\textperthousand}$  are derived from the mixed sources from fossil fuel and biomass combustion in East Asia. Due to the limited number of carbon isotopic measurements of  $\text{C}_6$ , its seasonality is not discussed here.

$\delta^{13}\text{C}$  values of  $\text{C}_9$  diacid ranged from  $-37.9\text{\textperthousand}$  to  $-21.0\text{\textperthousand}$  with a mean of  $-27.6 \pm 5.3\text{\textperthousand}$ , which are much smaller than those of  $\text{C}_2$ – $\text{C}_4$  and  $\text{C}_6$  diacids but are very close to those found for the identified fatty acids (mean:  $-26.9\text{\textperthousand}$ , see below). Indeed, previous studies show that  $\text{C}_9$  diacid can be produced by atmospheric oxidation of unsaturated fatty acids containing a double bond predominantly at the C-9 position (e.g., oleic and linoleic acids), which are emitted from either terrestrial higher plants or marine phytoplankton [Kawamura and Gagosian, 1987] and/or biomass burning [Ballentine et al., 1998]. It should be noted that the  $\delta^{13}\text{C}$  values of organic aerosols derived from terrestrial  $\text{C}_3$  plants and biomass burning are generally smaller than those from marine biological sources. The decreased  $\delta^{13}\text{C}$  values in spring and winter could be associated with long-range transport of organic aerosols emitted from enhanced biomass burning in East China [Liu et al., 2013; Zhang et al., 2014]. Therefore, the observed  $\delta^{13}\text{C}$  value of  $\text{C}_9$  suggests that a major fraction of  $\text{C}_9$  diacid, except for some spring and winter samples, is derived from photochemical oxidation of unsaturated fatty acids of marine biota origin, although the contributions from the terrestrial  $\text{C}_3$  plant and biomass burning from East China are also considerably important. This interpretation is consistent with the previously proposed formation pathway of Kawamura and Gagosian [1987].

Similarly, the  $\text{C}_5$  diacid is also depleted in  $^{13}\text{C}$  compared to longer-chain diacids and fatty acids; hence, it is likely that atmospheric oxidation of unsaturated fatty acids and/or degradation of higher diacids is a major source of

the C<sub>5</sub> diacid. Lower  $\delta^{13}\text{C}$  values were found for kC<sub>7</sub> compared to C<sub>9</sub>, which is due to isotope fractionation during its photochemical production from pimelic acid and/or monocarboxylic acids containing an additional oxo group at the C-4 position as the heavier isotope would be preferably retained in the particulate phase [Kawamura *et al.*, 2010].

Phthalic acid (Ph) and its isomer terephthalic acid (tPh) show smaller  $\delta^{13}\text{C}$  values (mean:  $-24.7 \pm 2.3\text{\textperthousand}$ ) than those of the C<sub>2</sub>-C<sub>4</sub> diacids but higher than that of the C<sub>9</sub> diacid. Previous studies suggest that Ph is unlikely to be produced by biogenic emissions but can be emitted from anthropogenic sources and/or produced by secondary oxidation of polycyclic aromatic hydrocarbons (PAHs) such as naphthalene, which are mainly derived from coal and biofuel combustion in source regions of East China [Kautzman *et al.*, 2010; Kawamura and Kaplan, 1987; Kawamura and Yasui, 2005; Wang *et al.*, 2006].  $^{13}\text{C}$  composition in Ph was within the range (i.e.,  $-27.1\text{\textperthousand}$  to  $-22.6\text{\textperthousand}$ ) of those in PAHs in source regions [Guillon *et al.*, 2013; Peng *et al.*, 2006]. tPh can be directly produced from burning plastic wastes [Wang *et al.*, 2012]. The similarity of  $\delta^{13}\text{C}$  in Ph and tPh implies a similar stable isotopic signature for organic aerosols emitted from both biomass and plastic waste burning. The  $\delta^{13}\text{C}$  features in C<sub>6</sub>, C<sub>9</sub>, and Ph diacids validate the previous findings that C<sub>6</sub> and Ph or tPh could be used as anthropogenic tracers, whereas C<sub>9</sub> is a good proxy of biogenic emissions.

### 3.3. $\delta^{13}\text{C}$ Values of Oxocarboxylic Acids, Tricarboxylic Acid, and $\alpha$ -Dicarbonyls

Similar to dicarboxylic acids, a general decrease of  $\delta^{13}\text{C}$  values in oxocarboxylic acids is observed with an increase in carbon numbers (Table 1 and Figure 2).  $\omega\text{C}_2$  shows the largest  $\delta^{13}\text{C}$  value ( $-13.8 \pm 4.7\text{\textperthousand}$ ) followed by  $\omega\text{C}_3$  ( $-17.7 \pm 7.4\text{\textperthousand}$ ) and Pyr ( $19.4 \pm 4.1\text{\textperthousand}$ ) or  $\omega\text{C}_4$  ( $-20.0 \pm 6.0\text{\textperthousand}$ ), whereas  $\omega\text{C}_7$ ,  $\omega\text{C}_8$ , and  $\omega\text{C}_9$  display the smallest values (mean:  $-23.0 \pm 3.2\text{\textperthousand}$ ). Because both the  $\omega\text{C}_2$  and C<sub>2</sub> diacids have relatively higher  $\delta^{13}\text{C}$  values, it is very likely that the C<sub>2</sub> diacid in Gosan aerosols is largely produced by aqueous phase oxidation of  $\omega\text{C}_2$  in aerosols (see section 3.4.). Low  $^{13}\text{C}$  values were observed for citric acid (mean:  $-27.8 \pm 4.2\text{\textperthousand}$ ), which is associated with its biogenic origins such as tangerine fruits with a typical  $^{13}\text{C}$  of  $-28.0 \pm 1.0\text{\textperthousand}$  [Jung and Kawamura, 2011]. Longer-chain oxoacids such as  $\omega\text{C}_8$  and  $\omega\text{C}_9$  can be produced by the photochemical oxidation of unsaturated fatty acids of terrestrial and/or marine plant [Kawamura and Gagosian, 1987]. Indeed,  $^{13}\text{C}$  is slightly less depleted in  $\omega\text{C}_7$ ,  $\omega\text{C}_8$ , and  $\omega\text{C}_9$  than in fatty acids (see below), likely because of isotope fractionation during photochemical production of pre-aged (or  $^{13}\text{C}$ -enriched) longer-chain oxocarboxylic acids from their major precursors such as unsaturated fatty acids. Another explanation could be that a substantial inverse isotope effect may be included in a reaction in formation of oxoacids from unsaturated fatty acids, although such a mechanism has not yet been reported. Both explanations need future experimental and field studies.

Glyoxal (Gly) and methylglyoxal (mGly) are two  $\alpha$ -dicarbonyls detected in this study. They are produced from oxidation of biogenic (e.g., isoprene) and anthropogenic volatile organic compounds (e.g., alkenes and aromatic hydrocarbons) in the atmosphere [Fu *et al.*, 2008]. It is of interest to note that a strong  $^{13}\text{C}$  enrichment is found for both Gly and MeGly with  $\delta^{13}\text{C}$  means of  $-13.5 \pm 5.2\text{\textperthousand}$  and  $-18.6 \pm 5.4\text{\textperthousand}$ , respectively. To our best knowledge, stable carbon isotope ratios of MeGly have not been reported before. However, previous studies found that the  $\delta^{13}\text{C}$  values of Gly respectively averaged  $-23.7 \pm 4.8\text{\textperthousand}$  to  $-20.2 \pm 3.9\text{\textperthousand}$  for aerosols collected in continental sites of Sapporo, Japan [Aggarwal and Kawamura, 2008] and Xi'an, China [Wang *et al.*, 2012], which are much smaller than our results.

A significant enrichment of  $^{13}\text{C}$  is observed for Gly and MeGly, which could be attributed to isotopic fractionation during photochemical oxidation and/or gas-particle partitioning. Unfortunately, there are no data reported on the kinetic isotopic effect for either of the processes, although it has been investigated for the photochemical oxidation of isoprene [Rudolph *et al.*, 2003], which has been proposed as a major precursor of the smallest  $\alpha$ -dicarbonyls (glyoxal) in the atmosphere [Fu *et al.*, 2008]. In contrast to such enrichment of  $^{13}\text{C}$  in Gly and MeGly,  $\delta^{13}\text{C}$  values are much lower in isoprene directly emitted from vegetation with typical values from  $-32\text{\textperthousand}$  to  $-27\text{\textperthousand}$  [Affek and Yakir, 2003; Rudolph *et al.*, 2003]. However, substantial enrichment of  $^{13}\text{C}$  of isoprene ( $\delta^{13}\text{C}$  value:  $-16.8\text{\textperthousand}$ ) has been reported at sites located remote from isoprene emitting vegetation due to isotope fractionation associated with the reaction with OH radicals [Rudolph *et al.*, 2003]. Similarly, the  $\delta^{13}\text{C}$  values of ethane over the open ocean generally have higher values due to the kinetic isotopic fractionation during atmospheric processing during long-range atmospheric transport [Saito *et al.*, 2011].

Another explanation of  $^{13}\text{C}$  enrichment in Gly and MeGly could be isotope fractionation during their atmospheric production. A chamber study shows that  $\beta$ -pinene is progressively enriched with the heavier

carbon isotope due to the kinetic isotope effect during its ozonolysis [Fisseha *et al.*, 2009]. In addition, norpinone, one of the major oxidation products, was more enriched with  $^{13}\text{C}$  in the particle phase than in the gas phase due to gas-particle partitioning [Fisseha *et al.*, 2009]. Therefore, we could hypothesize that the strong  $^{13}\text{C}$  enrichment found in Gly and MeGly in the particle phase is likely caused by the kinetic isotope effect during the aqueous phase chemical processes associated with their high water solubility and gas-particle partitioning given the preferential volatilization of the lighter isotope in the two semivolatile organic compounds. Indeed,  $^{13}\text{C}$  values in Gly are generally higher than those in MeGly (see Table 1 and Figure 2), which is likely due to higher isotope fractionation associated with higher vapor pressure and smaller carbon numbers in Gly compared to MeGly. Previous studies have provided evidences that kinetic isotope effects of a homologous series of light and aromatic hydrocarbons during the photochemical processing with OH radicals show significant increase with decreasing carbon numbers [Anderson *et al.*, 2004; Rudolph *et al.*, 2000]. Consequently, strong enrichment of  $^{13}\text{C}$  in Gly and MeGly could be explained by the secondary production from the oxidation of pre-aged isoprene and the other precursors with relatively higher  $^{13}\text{C}$  content.

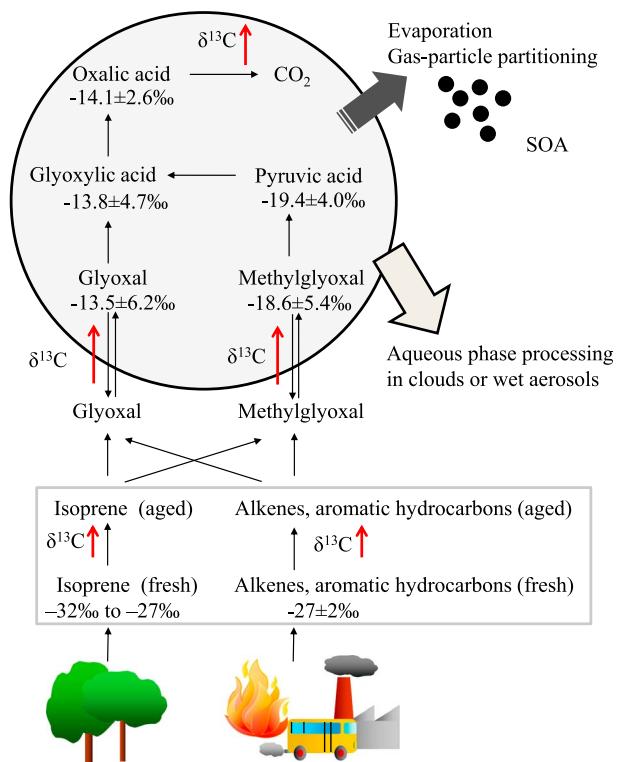
### 3.4. $\delta^{13}\text{C}$ Values of Low-Molecular Weight Fatty Acids

Low molecular weight (LMW) fatty acids can be derived from vascular plants, microbial sources, and marine phytoplankton [Kawamura *et al.*, 2003; Wang and Kawamura, 2005]. The  $\delta^{13}\text{C}$  values of LMW fatty acids varied from  $-32.1\text{\textperthousand}$  to  $-23.7\text{\textperthousand}$  with a mean of  $-26.9 \pm 1.5\text{\textperthousand}$  (Figure 2), which are comparable to those ( $-25.8\text{\textperthousand}$ ) found in fatty acids from Chichijima Island over the western North Pacific [Fang *et al.*, 2002]. Organic aerosols with a direct marine origin are characterized by a higher  $\delta^{13}\text{C}$  values of  $\sim -21 \pm 2\text{\textperthousand}$  [Cachier *et al.*, 1986], whereas LMW fatty acids ( $\text{C}_{14:0}$ ,  $\text{C}_{16:0}$ , and  $\text{C}_{18:0}$  and  $\text{C}_{18:1}$ ) in C3 higher plants have lower  $^{13}\text{C}$  values ranging from  $-36.4\text{\textperthousand}$  to  $-34.9\text{\textperthousand}$  [Matsumoto *et al.*, 2007]. No significant seasonal trend is found for the  $\delta^{13}\text{C}$  values (standard derivation: 1.5%) of the identified fatty acids throughout the year, suggesting a consistent source of fatty acids from the mixed contribution of marine biota and higher plants. Assuming the end-members of  $\delta^{13}\text{C}$  values for terrestrial C3 plants ( $-33.2 \pm 2.0\text{\textperthousand}$ ) [Matsumoto *et al.*, 2007] and marine phytoplankton ( $-21 \pm 2\text{\textperthousand}$ ) [Cachier *et al.*, 1986], we estimated that marine contribution for LMW fatty acids is on average  $59 \pm 3\%$  with maximum in summer (64%) and minimum in winter (56%).

### 3.5. Implications of Enrichment of $^{13}\text{C}$ in Oxalic Acid, Glyoxylic Acid, Pyruvic Acid, Glyoxal, and Methylglyoxal

As discussed in previous sections,  $\delta^{13}\text{C}$  values are generally higher for shorter-chain diacids and related compounds including  $\text{C}_2$ ,  $\omega\text{C}_2$ , Pyr, Pyr, Gly, and MeGly compared to other organic acids identified such as longer-chain diacids and fatty acids, which supports our hypothesis that  $\text{C}_2$  is not from photochemical breakdown of longer-chain diacids or fatty acid. However, previous studies have revealed that oxalic acid is a major oxidation product of longer-chain diacids and other precursors such as  $\omega\text{C}_2$  and Gly [Carlton *et al.*, 2007; Kawamura *et al.*, 1996; Lim *et al.*, 2013]. Our measurements suggest that oxidation of longer-chain diacids is unlikely a major formation pathway of oxalic acid in Gosan aerosol, because  $^{13}\text{C}$  should be more depleted in oxalic acid than in longer diacids if this is the case. This  $^{13}\text{C}$ -enrichment suggests that  $\alpha$ -dicarbonyls (Gly and MeGly), oxoacids ( $\omega\text{C}_2$  and Pyr), and the  $\text{C}_2$  diacid may have a close link in the photochemical pathways as described in many other field and laboratory experiments [Carlton *et al.*, 2007; Lim *et al.*, 2013] (see Figure 6). Several laboratory and photochemical model studies have recently suggested that the uptake of these  $\alpha$ -dicarbonyls by aqueous aerosols or cloud droplets, followed by the oxidation of their intermediate products such as glycolic, glyoxylic, and pyruvic acids, and the subsequent evaporation could be a significant source of oxalic acid and related secondary organic aerosols [Carlton *et al.*, 2007; Lim *et al.*, 2013]. As a result of aqueous phase oxidation of Gly and MeGly,  $^{13}\text{C}$  is enriched in their products such as  $\omega\text{C}_2$ , Pyr, and  $\text{C}_2$ .

In addition, subsequent gas-particle partitioning after droplet evaporation could further lead to an enrichment of the heavier isotope in these semivolatile organic compounds in the aerosol phase. The  $\delta^{13}\text{C}$  values of the measured organic acids and  $\alpha$ -dicarbonyls in this study suggest that aqueous phase oxidation of water-soluble  $\alpha$ -dicarbonyls (i.e., Gly and MeGly) is an important source of oxalic acid in the atmosphere relative to the degradation of higher homologues of diacids, which are produced by the oxidation of unsaturated fatty acids. It should be noted that the  $\delta^{13}\text{C}$  values of  $\text{C}_2$ ,  $\omega\text{C}_2$ , Pyr, Pyr, Gly, and MeGly are consistently higher than those reported in previous studies (see sections 3.2 and 3.3). These results indicate that organic aerosols in the Gosan site located under the East Asian continental air-mass outflow are extensively photochemically aged in association with increasing regional



**Figure 6.** Aqueous phase productions of oxalic acid and intermediates such as glyoxylic and pyruvic acids from glyoxal and methylglyoxal (modified from Carlton *et al.* [2007] and Lim *et al.* [2013]). Shaded area indicates an aqueous phase processing in clouds or wet aerosols, whereas nonshared area indicates a gas phase reaction. The numbers indicate the average stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) of oxalic acid, glyoxylic acid, pyruvic acid, glyoxal, and methylglyoxal measured for Gosan aerosols in this study. The  $\delta^{13}\text{C}$  values of isoprene, alkenes, and aromatic hydrocarbons are derived from the other studies [Affek and Yakir, 2003; Goldstein and Shaw, 2003; Rudolph *et al.*, 2003]. Red arrows denote enrichment (increasing  $\delta^{13}\text{C}$ ) during atmospheric processing.

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atmospheric oxidation capacity; a finding may be subject to further constraints by conducting long-term study of stable carbon isotope compositions of organic acids and related compounds in aerosols from East Asia.

#### 4. Summary

Based on the compound-specific stable carbon isotopic measurements of LMW dicarboxylic acids and related compounds in the aerosols from the Gosan background site in East Asia, a general decrease of  $\delta^{13}\text{C}$  values is observed with an increase in carbon chain length for both the homologues of dicarboxylic acids and oxocarboxylic acids. Particle phase glyoxal and methylglyoxal are more enriched in  $^{13}\text{C}$  compared to freshly emitted isoprene and other precursors such as alkenes and aromatic hydrocarbons, as a consequence of isotopic fractionation during particle phase production from pre-aged precursors. Such an isotopic enrichment is also consistently observed for oxalic, glyoxylic, and pyruvic acids compared to other organic acids identified, which can be explained by the kinetic isotope effects during aqueous phase processing and the subsequent gas-particle partitioning after the evaporation of clouds or wet aerosols.

The stable carbon isotopic results also provide evidence that oxalic acid in aerosols from the Gosan site with the East Asian continental outflow is mainly produced from atmospheric oxidation of glyoxylic acid and pyruvic acid, which are the key aqueous phase intermediates from glyoxal and methylglyoxal. This study demonstrates that compound-specific stable isotope measurements of organic acids and related compounds allow a better understanding of source and atmospheric processing of organic aerosols. Further laboratory experiments are encouraged to study kinetic isotope effects during the aqueous phase oxidation of isoprene, which is one of the most important precursors of small organic acids and  $\alpha$ -carbonyls. These experiments could provide direct constraints on the extent of isotope fractionations of different organic molecules produced during the aqueous processing. Such a data set could be directly incorporated into atmospheric chemical models and thus be used to estimate the extent of atmospheric processing of organic aerosols.

#### References

- Affek, H. P., and D. Yakir (2003), Natural abundance carbon isotope composition of isoprene reflects incomplete coupling between isoprene synthesis and photosynthetic carbon flow, *Plant Physiol.*, 131(4), 1727–1736.
- Aggarwal, S. G., and K. Kawamura (2008), Molecular distributions and stable carbon isotopic compositions of dicarboxylic acids and related compounds in aerosols from Sapporo, Japan: Implications for photochemical aging during long-range atmospheric transport, *J. Geophys. Res.*, 113, D14301, doi:10.1029/2007JD009365.
- Anderson, R. S., R. Iannone, A. E. Thompson, J. Rudolph, and L. Huang (2004), Carbon kinetic isotope effects in the gas-phase reactions of aromatic hydrocarbons with the OH radical at 296  $\pm$  4 K, *Geophys. Res. Lett.*, 31, L15108, doi:10.1029/2004GL020089.

- Ballantine, D. C., S. A. Macko, and V. C. Turekian (1998), Variability of stable carbon isotopic compositions in individual fatty acids from combustion of  $C_4$  and  $C_3$  plants: Implications for biomass burning, *Chem. Geol.*, 152(1–2), 151–161.
- Birch, M. E., and R. A. Cary (1996), Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust, *Aerosol Sci. Technol.*, 25(3), 221–241.
- Bond, T. C., D. G. Streets, K. F. Yarber, S. M. Nelson, J. H. Woo, and Z. Klimont (2004), A technology-based global inventory of black and organic carbon emissions from combustion, *J. Geophys. Res.*, 109, D14203, doi:10.1029/2003JD003697.
- Cachier, H., P. Buat-Ménard, M. Fontugne, and R. Chesselet (1986), Long-range transport of continentally-derived particulate carbon in the marine atmosphere: Evidence from stable carbon isotope studies, *Tellus B*, 38(3–4), 161–177.
- Carlton, A. G., B. J. Turpin, H. J. Lim, K. E. Altieri, and S. Seitzinger (2006), Link between isoprene and secondary organic aerosol (SOA): Pyruvic acid oxidation yields low volatility organic acids in clouds, *Geophys. Res. Lett.*, 33, L06822, doi:10.1029/2005GL025374.
- Carlton, A. G., B. J. Turpin, K. E. Altieri, S. Seitzinger, A. Reff, H. J. Lim, and B. Ervens (2007), Atmospheric oxalic acid and SOA production from glyoxal: Results of aqueous photooxidation experiments, *Atmos. Environ.*, 41(35), 7588–7602.
- Carmichael, G. R., et al. (2009), Asian aerosols: Current and year 2030 distributions and implications to human health and regional climate change, *Environ. Sci. Technol.*, 43(15), 5811–5817.
- de Gouw, J. A., et al. (2004), Chemical composition of air masses transported from Asia to the U. S. West Coast during ITCT 2K2: Fossil fuel combustion versus biomass-burning signatures, *J. Geophys. Res.*, 109, D23S20, doi:10.1029/2003JD004202.
- Fang, J. S. E., K. Kawamura, Y. Ishimura, and K. Matsumoto (2002), Carbon isotopic composition of fatty acids in the marine aerosols from the Western North Pacific: Implication for the source and atmospheric transport, *Environ. Sci. Technol.*, 36(12), 2598–2604.
- Fisseha, R., H. Spahn, R. Wegener, T. Hohaus, G. Brasse, H. Wissel, R. Tillmann, A. Wahner, R. Koppmann, and A. Kiendler-Scharr (2009), Stable carbon isotope composition of secondary organic aerosol from beta-pinene oxidation, *J. Geophys. Res.*, 114, D02304, doi:10.1029/2008JD011326.
- Fu, T. M., D. J. Jacob, F. Wittrock, J. P. Burrows, M. Vrekoussis, and D. K. Henze (2008), Global budgets of atmospheric glyoxal and methylglyoxal, and implications for formation of secondary organic aerosols, *J. Geophys. Res.*, 113, D15303, doi:10.1029/2007JD009505.
- Goldstein, A. H., and S. L. Shaw (2003), Isotopes of volatile organic compounds: An emerging approach for studying atmospheric budgets and chemistry, *Chem. Rev.*, 103(12), 5025–5048.
- Guillon, A., K. Le Menach, P. M. Flaud, N. Marchand, H. Budzinski, and E. Villenave (2013), Chemical characterization and stable carbon isotopic composition of particulate Polycyclic Aromatic Hydrocarbons issued from combustion of 10 Mediterranean woods, *Atmos. Chem. Phys.*, 13(5), 2703–2719.
- Hatakeyama, S., M. Ohno, J. H. Weng, H. Takagi, and H. Akimoto (1987), Mechanism for the formation of gaseous and particulate products from ozone-cycloalkene reactions in air, *Environ. Sci. Technol.*, 21(1), 52–57.
- Ho, K. F., J. J. Cao, S. C. Lee, K. Kawamura, R. J. Zhang, J. C. Chow, and J. G. Watson (2007), Dicarboxylic acids, ketocarboxylic acids, and dicarbonyls in the urban atmosphere of China, *J. Geophys. Res.*, 112, D22S27, doi:10.1029/2006JD008011.
- Ho, K. F., S. C. Lee, S. S. H. Ho, K. Kawamura, E. Tachibana, Y. Cheng, and T. Zhu (2010), Dicarboxylic acids, ketocarboxylic acids, alpha-dicarbonyls, fatty acids, and benzoic acid in urban aerosols collected during the 2006 Campaign of Air Quality Research in Beijing (CAREBeijing-2006), *J. Geophys. Res.*, 115, D19312, doi:10.1029/2009JD013304.
- Huang, R. J., et al. (2014), High secondary aerosol contribution to particulate pollution during haze events in China, *Nature*, 514(7521), 218–222.
- Jung, J. S., and K. Kawamura (2011), Enhanced concentrations of citric acid in spring aerosols collected at the Gosan background site in East Asia, *Atmos. Environ.*, 45(30), 5266–5272.
- Kautzman, K. E., J. D. Surratt, M. N. Chan, A. W. H. Chan, S. P. Hersey, P. S. Chhabra, N. F. Dalleska, P. O. Wennberg, R. C. Flagan, and J. H. Seinfeld (2010), Chemical composition of gas- and aerosol-phase products from the photooxidation of naphthalene, *J. Phys. Chem. A*, 114(2), 913–934.
- Kawamura, K., and I. R. Kaplan (1987), Motor exhaust emissions as a primary source for dicarboxylic acids in Los Angeles ambient air, *Environ. Sci. Technol.*, 21(1), 105–110.
- Kawamura, K., and K. Ikushima (1993), Seasonal-changes in the distribution of dicarboxylic-acids in the urban atmosphere, *Environ. Sci. Technol.*, 27(10), 2227–2235.
- Kawamura, K., and O. Yasui (2005), Diurnal changes in the distribution of dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban Tokyo atmosphere, *Atmos. Environ.*, 39(10), 1945–1960.
- Kawamura, K., and R. B. Gagosian (1987), Implications of omega-oxocarboxylic acids in the remote marine atmosphere for photooxidation of unsaturated fatty-acids, *Nature*, 325(6102), 330–332.
- Kawamura, K., and S. Bikkina (2016), A review of dicarboxylic acids and related compounds in atmospheric aerosols: Molecular distributions, sources and transformation, *Atmos. Res.*, 170, 140–160.
- Kawamura, K., and T. Watanabe (2004), Determination of stable carbon isotopic compositions of low molecular weight dicarboxylic acids and ketocarboxylic acids in atmospheric aerosol and snow samples, *Anal. Chem.*, 76(19), 5762–5768.
- Kawamura, K., H. Kasukabe, and L. A. Barrie (1996), Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: One year of observations, *Atmos. Environ.*, 30(10–11), 1709–1722.
- Kawamura, K., Y. Ishimura, and K. Yamazaki (2003), Four years' observations of terrestrial lipid class compounds in marine aerosols from the western North Pacific, *Global Biogeochem. Cycles*, 17(1), 1003, doi:10.1029/2001GB001810.
- Kawamura, K., H. Kasukabe, and L. A. Barrie (2010), Secondary formation of water-soluble organic acids and  $\alpha$ -dicarbonyls and their contributions to total carbon and water-soluble organic carbon: Photochemical aging of organic aerosols in the Arctic spring, *J. Geophys. Res.*, 115, D21306, doi:10.1029/2010JD014299.
- Kumar, P. P., K. Broekhuizen, and J. P. D. Abbatt (2003), Organic acids as cloud condensation nuclei: Laboratory studies of highly soluble and insoluble species, *Atmos. Chem. Phys.*, 3, 509–520.
- Lim, H. J., A. G. Carlton, and B. J. Turpin (2005), Isoprene forms secondary organic aerosol through cloud processing: Model simulations, *Environ. Sci. Technol.*, 39(12), 4441–4446.
- Lim, Y. B., Y. Tan, and B. J. Turpin (2013), Chemical insights, explicit chemistry, and yields of secondary organic aerosol from OH radical oxidation of methylglyoxal and glyoxal in the aqueous phase, *Atmos. Chem. Phys.*, 13(17), 8651–8667.
- Limbeck, A., and H. Puxbaum (1999), Organic acids in continental background aerosols, *Atmos. Environ.*, 33(12), 1847–1852.
- Liu, D., J. Li, Y. Zhang, Y. Xu, X. Liu, P. Ding, C. Shen, Y. Chen, C. Tian, and G. Zhang (2013), The use of levoglucosan and radiocarbon for source apportionment of  $PM_{2.5}$  carbonaceous aerosols at a background site in East China, *Environ. Sci. Technol.*, 47(18), 10,454–10,461.
- Matsumoto, K., K. Kawamura, M. Uchida, and Y. Shibata (2007), Radiocarbon content and stable carbon isotopic ratios of individual fatty acids in subsurface soil: Implication for selective microbial degradation and modification of soil organic matter, *Geochem. J.*, 41(6), 483–492.
- Mkoma, S. L., K. Kawamura, and E. Tachibana (2014), Stable carbon isotopic compositions of low-molecularweight dicarboxylic acids, glyoxylic acid and glyoxal in tropical aerosols: Implications for photochemical processes of organic aerosols, *Tellus B*, 66, 23,702.

- Narukawa, M., K. Kawamura, N. Takeuchi, and T. Nakajima (1999), Distribution of dicarboxylic acids and carbon isotopic compositions in aerosols from 1997 Indonesian forest fires, *Geophys. Res. Lett.*, 26(20), 3101–3104, doi:10.1029/1999GL010810.
- Nepotchatykh, O. V., and P. A. Ariya (2002), Degradation of dicarboxylic acids ( $C_2$ - $C_9$ ) upon liquid-phase reactions with  $O_3$  and its atmospheric implications, *Environ. Sci. Technol.*, 36(15), 3265–3269.
- Pavuluri, C. M., and K. Kawamura (2012), Evidence for 13-carbon enrichment in oxalic acid via iron catalyzed photolysis in aqueous phase, *Geophys. Res. Lett.*, 39, L03802, doi:10.1029/2011GL050398.
- Pavuluri, C. M., K. Kawamura, T. Swaminathan, and E. Tachibana (2011), Stable carbon isotopic compositions of total carbon, dicarboxylic acids and glyoxylic acid in the tropical Indian aerosols: Implications for sources and photochemical processing of organic aerosols, *J. Geophys. Res.*, 116, D18307, doi:10.1029/2011JD015617.
- Peng, C., M. N. Chan, and C. K. Chan (2001), The hygroscopic properties of dicarboxylic and multifunctional acids: Measurements and UNIFAC predictions, *Environ. Sci. Technol.*, 35(22), 4495–4501.
- Peng, L., Y. You, Z. P. Bai, T. Zhu, K. C. Xie, Y. C. Feng, and Z. Y. Li (2006), Stable carbon isotope evidence for origin of atmospheric polycyclic aromatic hydrocarbons in Zhengzhou and Urumchi, China, *Geochem. J.*, 40(3), 219–226.
- Rudolph, J., E. Czuba, and L. Huang (2000), The stable carbon isotope fractionation for reactions of selected hydrocarbons with OH-radicals and its relevance for atmospheric chemistry, *J. Geophys. Res.*, 105(D24), 29,329–29,346, doi:10.1029/2000JD900447.
- Rudolph, J., R. S. Anderson, K. V. Czapiewski, E. Czuba, D. Ernst, T. Gillespie, L. Huang, C. Rigby, and A. E. Thompson (2003), The stable carbon isotope ratio of biogenic emissions of isoprene and the potential use of stable isotope ratio measurements to study photochemical processing of isoprene in the atmosphere, *J. Atmos. Chem.*, 44(1), 39–55.
- Saito, T., O. Stein, U. Tsunogai, K. Kawamura, T. Nakatsuka, T. Gamo, and N. Yoshida (2011), Stable carbon isotope ratios of ethane over the North Pacific: Atmospheric measurements and global chemical transport modeling, *J. Geophys. Res.*, 116, D02308, doi:10.1029/2010JD014602.
- Spivakovsky, C. M., et al. (2000), Three-dimensional climatological distribution of tropospheric OH: Update and evaluation, *J. Geophys. Res.*, 105(D7), 8931–8980, doi:10.1029/1999JD901006.
- Timonen, H., M. Aurela, S. Carbone, K. Saarnio, S. Saarikoski, T. Makela, M. Kulmala, V. M. Kerminen, D. R. Worsnop, and R. Hillamo (2010), High time-resolution chemical characterization of the water-soluble fraction of ambient aerosols with PILS-TOC-IC and AMS, *Atmos. Meas. Tech.*, 3(4), 1063–1074.
- Turekian, V. C., S. A. Macko, and W. C. Keene (2003), Concentrations, isotopic compositions, and sources of size-resolved, particulate organic carbon and oxalate in near-surface marine air at Bermuda during spring, *J. Geophys. Res.*, 108(D5), 4157, doi:10.1029/2002JD002053.
- van Pinxteren, D., C. Neususs, and H. Herrmann (2014), On the abundance and source contributions of dicarboxylic acids in size-resolved aerosol particles at continental sites in central Europe, *Atmos. Chem. Phys.*, 14(8), 3913–3928.
- Wang, G. H., and K. Kawamura (2005), Molecular characteristics of urban organic aerosols from Nanjing: A case study of a mega-city in China, *Environ. Sci. Technol.*, 39(19), 7430–7438.
- Wang, G. H., K. Kawamura, S. Lee, K. F. Ho, and J. J. Cao (2006), Molecular, seasonal, and spatial distributions of organic aerosols from fourteen Chinese cities, *Environ. Sci. Technol.*, 40(15), 4619–4625.
- Wang, G. H., K. Kawamura, C. L. Cheng, J. J. Li, J. J. Cao, R. J. Zhang, T. Zhang, S. X. Liu, and Z. Z. Zhao (2012), Molecular distribution and stable carbon isotopic composition of dicarboxylic acids, ketocarboxylic acids, and alpha-dicarbonyls in size-resolved atmospheric particles from Xi'an City, China, *Environ. Sci. Technol.*, 46(9), 4783–4791.
- Wang, H. B., and K. Kawamura (2006), Stable carbon isotopic composition of low-molecular-weight dicarboxylic acids and ketoacids in remote marine aerosols, *J. Geophys. Res.*, 111, D07304, doi:10.1029/2005JD006466.
- Wang, Y., Y. Zhang, J. Hao, and M. Luo (2011), Seasonal and spatial variability of surface ozone over China: Contributions from background and domestic pollution, *Atmos. Chem. Phys.*, 11(7), 3511–3525.
- Widory, D., S. Roy, Y. Le Moullac, G. Gouplil, A. Cocherie, and C. Guerrot (2004), The origin of atmospheric particles in Paris: A view through carbon and lead isotopes, *Atmos. Environ.*, 38(7), 953–961.
- Yu, J. Z., X. F. Huang, J. H. Xu, and M. Hu (2005), When aerosol sulfate goes up, so does oxalate: Implication for the formation mechanisms of oxalate, *Environ. Sci. Technol.*, 39(1), 128–133.
- Zhang, Q., et al. (2007), Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, *Geophys. Res. Lett.*, 34, L13801, doi:10.1029/2007GL029979.
- Zhang, Q., et al. (2009), Asian emissions in 2006 for the NASA INTEX-B mission, *Atmos. Chem. Phys.*, 9(14), 5131–5153.
- Zhang, Y. L., et al. (2015), Fossil vs. non-fossil sources of fine carbonaceous aerosols in four Chinese cities during the extreme winter haze episode of 2013, *Atmos. Chem. Phys.*, 15(3), 1299–1312.
- Zhang, Y.-L., J. Li, G. Zhang, P. Zotter, R.-J. Huang, J.-H. Tang, L. Wacker, A. S. H. Prévôt, and S. Szidat (2014), Radiocarbon-based source apportionment of carbonaceous aerosols at a regional background site on Hainan Island, South China, *Environ. Sci. Technol.*, 48(5), 2651–2659.