Stable carbon isotopic compositions of low-molecular-weight dicarboxylic acids, oxocarboxylic acids...

DOI: 10.1002/2015JD024081

CITATIONS 3
READS 63

4 authors, including:

Yanlin Zhang
Nanjing University of Information Science & Technology

44 PUBLICATIONS 716 CITATIONS

SEE PROFILE
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\(^1\), Kimitaka Kawamura\(^1,3\), Fang Cao\(^2\), and Meehye Lee\(^4\)

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

Abstract

Stable carbon isotopic compositions (\( \delta^{13} \)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. \( \delta^{13} \)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 (C2, average \(-14.1\)‰), glyoxalic acid (\(-13.8\)‰), pyruvic acid (\(-19.4\)‰), glyoxal (\(-13.5\)‰), and methylglyoxal (\(-18.6\)‰) compared to other organic species (e.g., palmitic acid, \(-26.3\)‰), 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 \( \delta^{13} \)C values of C2 is positively correlated with C2 to organic carbon ratio, indicating that photochemical production of C2 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 glyoxal 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 \( \delta^{13} \)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 \( ^{13} \)C than malonic,
succinic, and glyoxylic acids. This difference suggests either that oxalic acid is formed from the oxidation of $^{13}$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 $^{13}$C [Aggarwal and Kawamura, 2008; Mkoma et al., 2014; Pavuluri and Kawamura, 2012]. In addition to dicarboxylic acids, a simultaneous measurement of $\delta^{13}$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 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°N, 126.10°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, ~65 m$^3$ 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°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°C until analysis. Field blank filters were collected every month.

2.2. Chemical Analysis

2.2.1. Mass Concentrations ofDicarboxylic Acids, Oxoacids, $\alpha$-Dicarbonyls, and Fatty Acids

Before $^{13}$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.
Table 1. Compound-Specific Stable Carbon Isotope Ratios (δ13C, ‰) of Low Molecular Weight Dicarboxylic Acids and Related Polar Compounds in Aerosols From Gosan Site

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
<th>Winter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range (SD)</td>
<td>Range (SD)</td>
<td>Range (SD)</td>
<td>Range (SD)</td>
</tr>
<tr>
<td>Oxalic acid, C2</td>
<td>-15.0 to 10.6</td>
<td>-12.6 (1.4)</td>
<td>-14.1 to 7.5</td>
<td>-11.5 (2.8)</td>
</tr>
<tr>
<td>Malonic acid, C3</td>
<td>-19.9 to 7.2</td>
<td>-14.9 (4.5)</td>
<td>-19 to 16</td>
<td>-17.5 (1.7)</td>
</tr>
<tr>
<td>Succinic acid, C4</td>
<td>-24.2 to 17.0</td>
<td>-19.4 (2.4)</td>
<td>-21.1 to 16.9</td>
<td>-19 (2.2)</td>
</tr>
<tr>
<td>Glutaric acid, C5</td>
<td>-28.8 to 21.9</td>
<td>-23.8 (2.3)</td>
<td>-40.9 to 23.3</td>
<td>-32.1 (12.5)</td>
</tr>
<tr>
<td>Adipic acid, C6</td>
<td>-20.7 to 18.7</td>
<td>-19.7 (1.4)</td>
<td>-24.9 to 24.9</td>
<td>-18.3</td>
</tr>
<tr>
<td>Terephthalic acid, tPh</td>
<td>-24.0 to 18.9</td>
<td>-21.4 (3.6)</td>
<td>-20.6</td>
<td>-20.6</td>
</tr>
<tr>
<td>Succinic acid, C3</td>
<td>-20.8 to 21.6</td>
<td>-24 (2.4)</td>
<td>-23.0</td>
<td>-23.0</td>
</tr>
<tr>
<td>Phthalic acid, Ph</td>
<td>-27.3 to -23</td>
<td>-24.4 (1.7)</td>
<td>NA</td>
<td>-26.5 to -21.4</td>
</tr>
<tr>
<td>Azelaic acid, C9</td>
<td>-36.8 to 22.5</td>
<td>-28.1 (6.5)</td>
<td>-25.4 to 24.1</td>
<td>-24.8 (0.7)</td>
</tr>
<tr>
<td>Glyoxylic acid, ωC2</td>
<td>-22.5 to 8.7</td>
<td>-14.7 (4.7)</td>
<td>-24.2 to 9.8</td>
<td>-15.9 (6.4)</td>
</tr>
<tr>
<td>Pyruvic acid, Pyr</td>
<td>-22.2 to 15.7</td>
<td>-19.1 (2.5)</td>
<td>-20.7 to 12.3</td>
<td>-17.6 (3.6)</td>
</tr>
<tr>
<td>3-Oxopropanoic acid, ωC3</td>
<td>-23.9 to 7.5</td>
<td>-18.0 (5.1)</td>
<td>-13.3 to 13.3</td>
<td>-13.3 (0)</td>
</tr>
<tr>
<td>4-Oxobutanolic acid, C4</td>
<td>-20.1 to 14.2</td>
<td>-17.9 (19)</td>
<td>-23.7 to 23.7</td>
<td>-23.7 (0)</td>
</tr>
<tr>
<td>7-Oxohexanoic acid, C7</td>
<td>-23.9 to 15.4</td>
<td>-21.3 (2.7)</td>
<td>-25.2 to 19.2</td>
<td>-22.6 (2.6)</td>
</tr>
<tr>
<td>8-Oxooctanoic acid, C8</td>
<td>-23.4 to 20.6</td>
<td>-25.7 (3.9)</td>
<td>-25.8 to 17.6</td>
<td>-21.8 (3.7)</td>
</tr>
<tr>
<td>Citric acid, C6</td>
<td>-33.0 to 23.4</td>
<td>-27.8 (4.2)</td>
<td>NA</td>
<td>-25.9 to 10.9</td>
</tr>
<tr>
<td>Glyoxal, Gly</td>
<td>-18.4 to 5.0</td>
<td>-10.6 (5.2)</td>
<td>-22.8 to 16.8</td>
<td>-20.8 (3.4)</td>
</tr>
<tr>
<td>Methylglyoxal, MeGly</td>
<td>-22.4 to 17.7</td>
<td>-18.1 (2.5)</td>
<td>-23.3 to 11.8</td>
<td>-17.7 (5.7)</td>
</tr>
<tr>
<td>3,4-Dihydroxybenzoic acid, C14</td>
<td>-33.0 to 23.4</td>
<td>-27.8 (4.2)</td>
<td>NA</td>
<td>-19.6 to 10.9</td>
</tr>
<tr>
<td>Palmitic acid, C16:0</td>
<td>-26.7 to 24.4</td>
<td>-25.8 (1)</td>
<td>-27.2 to 26.3</td>
<td>-26.9 (0.5)</td>
</tr>
<tr>
<td>Stearic acid, C18:0</td>
<td>-28.3 to 27.9</td>
<td>-28.1 (0.3)</td>
<td>-30.1 to 26.4</td>
<td>-27.8 (1.4)</td>
</tr>
<tr>
<td>Oleic acid, C18:1</td>
<td>-27.9 to 27.8</td>
<td>-27.9 (0.1)</td>
<td>-26.2 to -25.5</td>
<td>-26 (0.5)</td>
</tr>
</tbody>
</table>

*NA: not available.

[Ho et al., 2010; Kawamura and Ikushima, 1993]. Briefly, a filter aliquot of 1.54 to 3.08 cm² 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% BF₃/n-butanol to derivatize carboxyl group to dibutyl ester and oxo groups to dibutyo acetics.

The derivates were extracted with n-hexane, concentrated to near dryness, dissolved in n-hexane, and finally determined using a gas chromatography (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, α-Dicarboxyls, and Fatty Acids

Stable carbon isotopic compositions (δ13C) 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 μL of internal standard (n-C₁₃ alkane, -27.24‰) was spiked to an aliquot of the derivative samples. δ13C values of the derivatives relative to Pee Dee Belemnite were determined by GC-combustion-isotope ratio mass spectrometry (Thermo Delta V). The δ13C values were then calculated for free organic acids using an isotopic mass balance equation based on the measured δ13C values of derivatives and the derivatizing agent (BF₃/n-butanol). Prior to actual sample analysis, we confirmed that δ13C values of the working standards (a mixture of normal C₃₀ alkanes with 0.55-2.83 ng/μL) were equivalent to the theoretical values within an analytical error of <0.2‰. The difference in δ13C values of major compounds (i.e., C₂, C₃, C₄, Ph, ωC₂, Gly, and MeGly, see Table 1) for replicate analyses was generally <1‰ though the analytical accuracy was 2% for other species.
3. Results and Discussion

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

The statistical distributions of $\delta^{13}$C values of nine dicarboxylic acids (i.e., diacids including C$_2$, C$_3$, C$_4$, C$_5$, C$_6$, C$_9$, kC$_7$, tPh, and Ph), seven oxocarboxylic acids (i.e., oxoacids including $\omega$C$_2$, Pyr, $\omega$C$_3$, $\omega$C$_4$, $\omega$C$_7$, $\omega$C$_8$, and $\omega$C$_9$), one tricarboxylic acid (Cit), two $\alpha$-dicarbonyls (Gly and MeGly), and four fatty acids (C14:0, C16:0, C18:0, and C18:1) 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 $^{13}$C compared to longer-chain (i.e., more than four carbon numbers) diacids, oxocarboxylic acids, and fatty acids.

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

The $\delta^{13}$C values of the three most abundant diacids (C$_2$, C$_3$, and C$_4$, see Table 1) fall within the range of ~7.2 to ~24.2‰ with a mean of ~16.0 ± 3.8‰ (i.e., mean ± 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‰ for 2005) [Aggarwal and Kawamura, 2008], a marine site from Bermuda in the North Atlantic Ocean (mean: ~21.0‰ for 1998) [Turekian et al., 2003], an urban site in Xi’an, northern China (mean: ~21.6‰ for 2009) [Wang et al., 2012], a rural site in Morogoro, Tanzania (mean: ~20.2‰ for 2011) [Mkoma et al., 2014], and a tropical site (mean: ~20.3‰ for 2007) [Pavuluri et al., 2011]. However, the results are similar to or only slightly larger than those (mean: ~16.8‰ during 1994–1995) obtained in the remote marine aerosols from the western Pacific and Southern Ocean [Wang and Kawamura, 2006]. The relatively high $\delta^{13}$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 $\delta^{13}$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. C$_2$ (the smallest dicarboxylic acid in the aerosol phase) and C$_9$ (the largest dicarboxylic acid detected in this study) diacids show the largest and smallest mean $\delta^{13}$C values, respectively. On average, C$_2$ diacid (~14.1 ± 2.6‰) is most enriched in $^{13}$C followed by C$_3$ (~14.6 ± 3.8‰) and C$_4$ diacids (~19.2 ± 1.5‰) (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 $^{13}$C with increased photochemical aging/photolysis of C$_2$ or 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].
The increased $\delta^{13}C$ values in diacids can be controlled by the decarboxylation reaction by photochemical oxidation and atmospheric production from precursors. Laboratory studies show that the $^{13}C$ enrichment of C$_2$ during photolysis could be enhanced in the presence of Fe$^{3+}$ or Fe$^{2+}$ [Pavuluri and Kawamura, 2012]. Furthermore, C$_2$ could also be produced by oxidation of oC$_2$, which can apparently be supported by its strong $^{13}C$ enrichment (see section 3.2). The $^{13}C$ enrichment in the C$_2$ diacid is more pronounced during spring and summer than fall and winter (Table 1 and Figure 3) 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 C$_3$ and C$_4$ diacids (Figure 3). However, it is interesting to note that the $\delta^{13}C$ values of the C$_3$ diacid in the cold seasons (i.e., November to March) are larger than those found in the C$_2$ diacid, which has not yet been reported in other regions.

Figure 4 plots the differences in $\delta^{13}C$ values of C$_2$ and C$_3$ ($\Delta\delta^{13}C(C_3-C_2)$) as a function of the mass concentration ratio of C$_3$ and C$_2$ (C$_3$/C$_2$). Interestingly, $\Delta\delta^{13}C(C_3/C_2)$ is negatively correlated with the C$_3$/C$_2$ ratio ($R^2 = 0.59$, $t$ test $p < 0.05$), which indicates an enrichment of $^{13}C$ in remaining the C$_3$ diacid likely due to the photochemical degradation of C$_3$ diacid and/or the depletion of $^{12}C$ in the C$_2$ diacid. Indeed, photochemical conditions in the East Asian atmosphere are characterized by relatively low O$_3$ and OH concentrations during the cold seasons [Spivakovsky 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 C$_3$ diacid are 2–4 orders of magnitude larger than other dicarboxylic acids (e.g., C$_2$, C$_4$ to C$_9$ diacids) [Nepotchatykh and Ariya, 2002]. Hence, C$_3$ is preferentially degraded compared to C$_2$ and C$_4$ during the cold seasons and $^{12}C$ is therefore less depleted in the remaining C$_3$ due to larger isotopic fractionation.

However, an opposite trend was observed in spring and summer when O$_3$ and 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 C$_2$ from aged precursors and photolysis of C$_2$ in the presence of oxalate-iron complex could affect its isotopic composition. Both processes could further enhance $^{13}C$ enrichment of C$_2$. Indeed, Pavuluri and Kawamura [2012] revealed a substantial increase in $\delta^{13}C$ values in the C$_2$ diacid during photolysis of the oxalate-iron complex, in which they proposed that $^{12}C$-$^{12}C$ bonds in diacids decompose preferentially over $^{12}C$-$^{13}C$ 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.
As shown in Figure 5, the δ13C values of C2 and the C2 to OC ratio (i.e., C2/OC) display similar temporal variations with a positive correlation (r = 0.43, p < 0.05). This result indicates that 13C enrichment of C2 is due to the production of C2 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 C2, no significant correlation (p > 0.05) is found between the relative abundances of other diacids (i.e., C3 and C4) and their isotope compositions, suggesting that the difference in mechanisms of formation and decomposition of C2 and C3 (and C4) may affect their δ13C 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.

C6 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 13C by 2−7‰ has been reported for organic compounds derived from biomass burning relative to the unburned C3 plant [Ballentine et al., 1998], whereas organic aerosols emitted from fossil combustion have smaller δ13C values [Widory et al., 2004]. Thus, the relatively high δ13C values of C6 diacid ranging from −24.9 to −18.3‰ 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 C6, its seasonality is not discussed here.

δ13C values of C9 diacid ranged from −37.9‰ to −21.0‰ with a mean of −27.6 ± 5.3‰, which are much smaller than those of C2-C4 and C6 diacids but are very close to those found for the identified fatty acids (mean: −26.9‰, see below). Indeed, previous studies show that C9 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 δ13C values of organic aerosols derived from terrestrial C9 plants and biomass burning are generally smaller than those from marine biological sources. The decreased δ13C 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 δ13C value of C9 suggests that a major fraction of C9 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 C3 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 C5 diacid is also depleted in 13C 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 C5 diacid. Lower δ\textsuperscript{13}C values were found for kC\textsubscript{7} compared to C\textsubscript{9}, which is due to isotope fractionation during its photochemical production from pinic 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 δ\textsuperscript{13}C values (mean: −24.7 ± 2.3‰) than those of the C\textsubscript{2}–C\textsubscript{4} diacids but higher than that of the C\textsubscript{9} 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]. \textsuperscript{13}C composition in Ph was within the range (i.e., −27.1‰ to −22.6‰) 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 δ\textsuperscript{13}C in Ph and tPh implies a similar stable isotopic signature for organic aerosols emitted from both biomass and plastic waste burning. The δ\textsuperscript{13}C features in C\textsubscript{9}, C\textsubscript{10}, and Ph diacids validate the previous findings that C\textsubscript{9} and Ph or tPh could be used as anthropogenic tracers, whereas C\textsubscript{9} is a good proxy of biogenic emissions.

### 3.3. δ\textsuperscript{13}C Values of Oxocarboxylic Acids, Tricarboxylic Acid, and α-Dicarbonyls

Similar to dicarboxylic acids, a general decrease of δ\textsuperscript{13}C values in oxocarboxylic acids is observed with an increase in carbon numbers (Table 1 and Figure 2). \textit{ω}C\textsubscript{3} shows the largest δ\textsuperscript{13}C value (−13.8 ± 4.7‰) followed by \textit{ω}C\textsubscript{5} (−17.7 ± 7.4‰) and P\textit{yr} (19.4 ± 4.1‰) or \textit{ω}C\textsubscript{4} (−20.0 ± 6.0‰), whereas \textit{ω}C\textsubscript{7}, \textit{ω}C\textsubscript{8}, and \textit{ω}C\textsubscript{9} display the smallest values (mean: −23.0 ± 3.2‰). Because both the \textit{ω}C\textsubscript{2} and \textit{C}\textsubscript{2} diacids have relatively higher δ\textsuperscript{13}C values, it is very likely that the \textit{C}\textsubscript{2} diacid in Gosan aerosols is largely produced by aqueous phase oxidation of \textit{ω}C\textsubscript{2} in aerosols (see section 3.4). Low \textsuperscript{13}C values were observed for citric acid (mean: −27.8 ± 4.2‰), which is associated with its biogenic origins such as tangerine fruits with a typical \textsuperscript{13}C of −28.0 ± 1.0‰ [Jung and Kawamura, 2011]. Longer-chain oxoacids such as \textit{ω}C\textsubscript{8} and \textit{ω}C\textsubscript{9} can be produced by the photochemical oxidation of unsaturated fatty acids of terrestrial and/or marine plant [Kawamura and Gagosian, 1987]. Indeed, \textsuperscript{13}C is slightly less depleted in \textit{ω}C\textsubscript{7}, \textit{ω}C\textsubscript{8}, and \textit{ω}C\textsubscript{9} than in fatty acids (see below), likely because of isotope fractionation during photochemical production of pre-aged (or \textsuperscript{13}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 α-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 \textsuperscript{13}C enrichment is found for both Gly and MeGly with δ\textsuperscript{13}C means of −13.5 ± 5.2‰ and −18.6 ± 5.4‰, respectively. To our best knowledge, stable carbon isotope ratios of MeGly have not been reported before. However, previous studies found that the δ\textsuperscript{13}C values of Gly respectively averaged −23.7 ± 4.8‰ to −20.2 ± 3.9‰ 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 \textsuperscript{13}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 α-dicarbonyl (glyoxal) in the atmosphere [Fu et al., 2008]. In contrast to such enrichment of \textsuperscript{13}C in Gly and MeGly, δ\textsuperscript{13}C values are much lower in isoprene directly emitted from vegetation with typical values from −32‰ to −27‰ [Affek and Yakir, 2003; Rudolph et al., 2003]. However, substantial enrichment of δ\textsuperscript{13}C of isoprene (δ\textsuperscript{13}C value: −16.8‰) has been reported at sites located remote from isoprene emitting vegetation due to isotopic fractionation associated with the reaction with OH radicals [Rudolph et al., 2003]. Similarly, the δ\textsuperscript{13}C values of ethene 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 \textsuperscript{13}C enrichment in Gly and MeGly could be isotope fractionation during their atmospheric production. A chamber study shows that β-pinene is progressively enriched with the heavier
carbon isotope due to the kinetic isotope effect during its ozonolysis [Fisseha et al., 2009]. In addition, norpineone, one of the major oxidation products, was more enriched with $^{13}$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 $^{13}$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, $^{13}$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 $^{13}$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 $^{13}$C content.

### 3.4. $^{13}$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 $^{13}$C values of LMW fatty acids varied from $-32.1\%$ to $-23.7\%$ with a mean of $-26.9 \pm 1.5\%$ (Figure 2), which are comparable to those ($-25.8\%$) 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 $^{13}$C values of $-21 \pm 2\%$ [Cachier et al., 1986], whereas LMW fatty acids ($C_{14:0}, C_{16:0}$, and $C_{18:0}$ and $C_{18:1}$) in C3 higher plants have lower $^{13}$C values ranging from $-36.4\%$ to $-34.9\%$ [Matsumoto et al., 2007]. No significant seasonal trend is found for the $^{13}$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 $^{13}$C values for terrestrial C3 plants ($-33.2 \pm 2.0\%$) [Matsumoto et al., 2007] and marine phytoplankton ($-21 \pm 2\%$) [Cachier et al., 1986], we estimated that marine contribution for LMW fatty acids is on average 59 ± 3% with maximum in summer (64%) and minimum in winter (56%).

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

As discussed in previous sections, $^{13}$C values are generally higher for shorter-chain diacids and related compounds including $C_2$, $\omega C_2$, Pry, Pyr, Gly, and MeGly compared to other organic acids identified such as longer-chain diacids and fatty acids, which supports our hypothesis that $C_2$ 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 $\omega C_2$ 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 $^{13}$C should be more depleted in oxalic acid than in longer diacids if this is the case. This $^{13}$C enrichment suggests that $\alpha$-dicarboxyls (Gly and MeGly), oxoacids ($\omega C_2$ and Pry), and the $C_2$ 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 $\alpha$-dicarboxyls 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, $^{13}$C is enriched in their products such as $\omega C_2$, Pry, and $C_2$.

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 $^{13}$C values of the measured organic acids and $\alpha$-dicarboxyls in this study suggest that aqueous phase oxidation of water-soluble $\alpha$-dicarboxyls (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 $^{13}$C values of $C_2$, $\alpha C_2$, Pry, 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
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 isotope measurements of LMW dicarboxylic acids and related compounds in the aerosols from the Gosan background site in East Asia, a general decrease of δ13C 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 13C 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.

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 (δ13C) of oxalic acid, glyoxylic acid, pyruvic acid, glyoxal, and methylglyoxal measured for Gosan aerosols in this study. The δ13C 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 δ13C) during atmospheric processing.

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 α-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.

Acknowledgments

Data supporting the results presented in this paper are available in the supporting information. Additional data are available upon request from the corresponding author (dryanlinzhang@gmail.com). We acknowledge the financial support by the Japan Society for the Promotion of Science (JSPS) (Grant-in-Aid 1920405 and 24221001) and the Environment Research and Technology Development Fund (B-0903) from the Ministry of the Environment, Japan. Y.-L. Zhang also acknowledges partial financial support from the Swiss National Science Foundation and JSPS. We thank Philip Meyers from University of Michigan for English editing.

References


