

Stable carbon isotopic compositions of low-molecular-weight dicarboxylic acids, glyoxylic acid and glyoxal in tropical aerosols: implications for photochemical processes of organic aerosols

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ABSTRACT

Tropical aerosols of PM_{2.5} and PM₁₀ were collected at a rural site in Morogoro, Tanzania (East Africa), and analysed for stable carbon isotopic composition ($\delta^{13}\text{C}$) of dicarboxylic acids (C₂–C₉), glyoxylic acid (ωC_2) and glyoxal (Gly) using gas chromatography/isotope ratio mass spectrometer. PM_{2.5} samples showed that $\delta^{13}\text{C}$ of oxalic (C₂) acid are largest (mean, $-18.3 \pm 1.7\text{‰}$) followed by malonic (C₃, $-19.6 \pm 1.0\text{‰}$) and succinic (C₄, $-21.8 \pm 2.2\text{‰}$) acids, whereas those in PM₁₀ are a little smaller: $-19.9 \pm 3.1\text{‰}$ (C₂), $-20.2 \pm 2.7\text{‰}$ (C₃) and $-23.3 \pm 3.2\text{‰}$ (C₄). The $\delta^{13}\text{C}$ of C₂–C₄ diacids showed a decreasing trend with an increase in carbon numbers. The higher $\delta^{13}\text{C}$ values of oxalic acid can be explained by isotopic enrichment of ^{13}C in the remaining C₂ due to the atmospheric decomposition of oxalic acid or its precursors. $\delta^{13}\text{C}$ of ωC_2 and Gly that are precursors of oxalic acid also showed larger values (mean, -22.5‰ and -20.2‰ , respectively) in PM_{2.5} than those (-26.7‰ and -23.7‰) in PM₁₀. The $\delta^{13}\text{C}$ values of ωC_2 and Gly are smaller than those of C₂ in both PM_{2.5} and PM₁₀. On the other hand, azelaic acid (C₉; mean, -28.5‰) is more depleted in ^{13}C , which is consistent with the previous knowledge; that is, C₉ is produced by the oxidation of unsaturated fatty acids emitted from terrestrial higher plants. A significant enrichment of ^{13}C in oxalic acid together with its negative correlations with relative abundance of C₂ in total diacids and ratios of water-soluble organic carbon and organic carbon further support that a photochemical degradation of oxalic acid occurs during long-range transport from source regions.

Keywords: PM_{2.5} and PM₁₀, stable carbon isotope ratios, oxalic acid, diacids, glyoxylic acid, glyoxal, organic aerosols, Tanzania, East Africa

1. Introduction

Low-molecular-weight dicarboxylic acids and related compounds comprise a significant fraction of organic aerosols and can play an important role in atmospheric chemistry and radiative forcing of the Earth's climate (Saxena and Hildemann, 1996). Dicarboxylic acids and related polar compounds are largely produced by photochemical processes in the atmosphere (Kawamura et al., 1996; Fisseha et al., 2004), but they can also be generated from primary

sources including fossil fuel combustion (Kawamura and Kaplan, 1987) and biomass burning (Narukawa et al., 1999; Kundu et al., 2010). Photochemical oxidation and breakdown of relatively higher molecular weight diacids and other precursors are important sources of lower molecular weight diacids in the atmosphere (Kawamura and Yasui, 2005). The removal and mixing processes can affect the ambient concentrations of these compounds during long-range atmospheric transport (Mochida et al., 2003).

Different approaches have been applied to understand the sources of atmospheric aerosols as well as their long-range transport (Kawamura et al., 2000; Schmidt et al., 2004; Wang et al., 2006). Compound-specific stable carbon isotope analysis of lower molecular weight organic

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compounds has been used to determine the extent of photochemical processing and contribution of effective mixing process of the compounds in the atmosphere using the estimated kinetic isotope effect of target compound with OH radicals (Kawamura and Watanabe, 2004; Wang and Kawamura, 2006). Compound-specific stable carbon isotope ratios that are more specific in source identifications of higher molecular weight organic compounds have been applied in many scientific fields (e.g. Lichtfouse, 2000; Schmidt et al., 2004).

Photochemical processing of aerosols in the atmosphere largely affects the composition of water-soluble matter in aerosols. Their composition is important in controlling the ability of a particle to be activated as cloud condensation nuclei (CCN) (Sun and Ariya, 2006; Shilling et al., 2007). Because diacids and related polar compounds are largely produced by photochemical oxidation, compound-specific stable carbon isotope analysis of these compounds can be a useful tool for the assessment of photochemical aging of organic aerosols (Kawamura and Watanabe, 2004; Wang and Kawamura, 2006).

Previous studies have been conducted on stable carbon isotope ratios of water-soluble organic species in atmospheric aerosols (Kawamura and Watanabe, 2004; Irei et al., 2006; Aggarwal and Kawamura, 2008). However, little is known about the stable isotopes in tropical aerosols (Pavuluri et al., 2011), and no studies have been conducted in Africa. Here, we report for the first time the stable carbon isotopic compositions of low-molecular-weight (C_2 – C_9) diacids, glyoxylic acid (ωC_2) and glyoxal (Gly) in tropical aerosols ($PM_{2.5}$ and PM_{10}) collected at a rural background site in Tanzania, East Africa, in May through August 2011. Based on $\delta^{13}C$ data, we discuss the sources and atmospheric processing of aerosols during long-range transport to the sampling site. This study provides the first baseline data

sets of compound-specific stable carbon isotope analysis of water-soluble organic aerosols from East Africa.

2. Experimental

2.1. Aerosol sampling

Aerosol sampling was carried out at Morogoro (300 000 inhabitants, Fig. 1), a rural site about 200 km west of the coast of the Indian Ocean (Mkoma and Kawamura, 2013) where the city of Dar es Salaam, a business capital in Tanzania, locates. The $PM_{2.5}$ and PM_{10} low-volume samplers were deployed at a University campus of Sokoine University of Agriculture ($06^{\circ}47'40.8''S$, $37^{\circ}37'44.5''E$, altitude 504 m a.s.l). Aerosols were collected at 2.7 m above ground level using ‘Gent type’ samplers (flow rate $17.0 L min^{-1}$; Maenhaut et al., 1994) and pre-combusted ($450^{\circ}C$ for 4 h) quartz fibre filters (Pallflex 2500QAT-UP, 47 mm). A total of 10 samples of $PM_{2.5}$ and 20 set of PM_{10} samples with 2 field blanks for each were collected on approximately 24 h basis in 2011 from 30 May to 13 June (for $PM_{2.5}$) and 30 May to 8 August (for PM_{10}). Before and after sampling, the filters were placed in a pre-heated glass vial with a Teflon-lined screw cap and kept at $-20^{\circ}C$ during storage. The samples were transported to the atmospheric chemistry laboratory at the Institute of Low Temperature Science, Hokkaido University (Japan) and stored in a freezer at $-20^{\circ}C$ prior to analysis. All the procedures were strictly quality-controlled to avoid any possible contamination of the samples.

2.2. Determination of $\delta^{13}C$ of diacids, glyoxylic acid and glyoxal

Stable carbon isotopic compositions ($\delta^{13}C$) of low-molecular-weight dicarboxylic acids, glyoxylic acid and

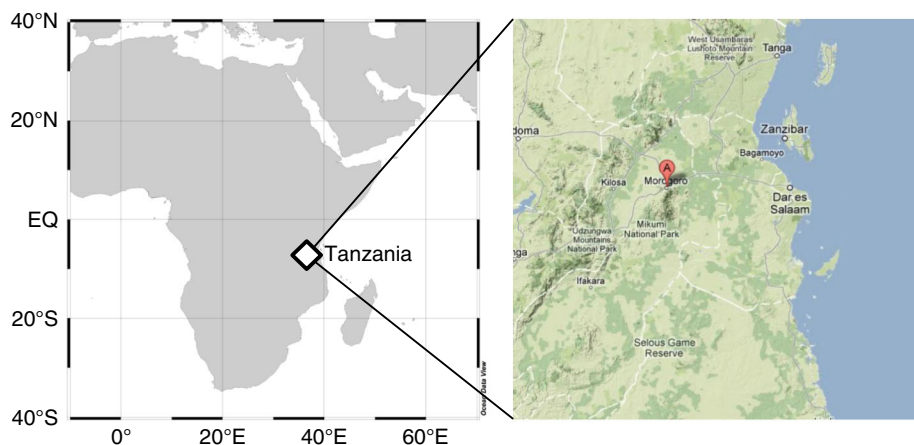


Fig. 1. Map showing the location of the sampling site in Morogoro, Tanzania.

glyoxal relative to Pee Dee Belemnite (PDB) were measured using the method developed by Kawamura and Watanabe (2004). Briefly, 2 μl of $n\text{-C}_{13}$ alkane (internal standard) was added to 40 μl of a portion previously derivatised for diacid analysis (Mkoma and Kawamura, 2013). The $\delta^{13}\text{C}$ of the derivatives were determined using a gas chromatograph (HP6890)/isotope ratio mass spectrometer (IRMS) (Finnigan MAT Delta Plus) system and calculated for free organic acids using an isotopic mass balance equation based on the measured $\delta^{13}\text{C}$ of the derivatives and the derivatising agent (1-butanol). Duplicate measurements for each sample were conducted and the difference in $\delta^{13}\text{C}$ for major diacids for replicate analyses was generally below 1%. However, for minor species, the analytical accuracy was $<2\%$.

The measurement of dicarboxylic acids, glyoxylic acid and glyoxal were done using a gas chromatography/flame ionisation detector (GC/FID) and GC/mass spectrometry (Kawamura and Yasui, 2005). Total concentrations of diacids were reported in a range of 289–362 ng m^{-3} . Those of oxoacids and α -dicarbonyls were 37.8–53.7 ng m^{-3} and 5.7–7.8 ng m^{-3} , respectively. Oxalic acid (C_2) was found as the most abundant diacid species followed by succinic and/or malonic acids whereas glyoxylic acid and glyoxal were the dominant oxoacid and α -dicarbonyl, respectively in both seasons in $\text{PM}_{2.5}$ and PM_{10} (Mkoma and Kawamura, 2013). The concentration of organic carbon (OC) was measured using a Sunset Laboratory carbon analyser following the method described in Wang et al. (2005) whereas water-soluble organic carbon (WSOC) was measured using a Shimadzu carbon analyser (TOC- V_{CSH}) (Miyazaki et al., 2011).

2.3. Meteorology and backward air mass trajectories

During the campaigns, meteorological parameters including ambient temperature, relative humidity and precipitation were recorded. The average ambient temperature was 25.0°C with minimum of 21.1°C and maximum of 29.1°C . The daily average relative humidity ranged from 65 to 96% in the morning hours and from 41 to 60% in the afternoon. The prominent wind pattern during sampling days was characterised by the south easterly (SE) monsoons with daytime average wind speed of 7.8 m s^{-1} . The aerosol samplings were conducted mostly in days without rain or with a very weak rain.

To characterise the air masses encountered at Morogoro during the campaign, 5-d back trajectory analyses were performed for each of the samples using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model of the NOAA/ARL (<http://ready.arl.noaa.gov/HYSPLIT.php>; Draxler and Rolph, 2012). The isentropic backward trajectories for 24 h samples indicated that the air masses in Morogoro were influenced by regional air masses from the Indian Ocean mixed with those from continental Madagascar, Mozambique and Tanzania (Fig. 2).

3. Results and discussion

3.1. Stable carbon isotopic compositions of dicarboxylic acids, glyoxylic acid and glyoxal

Tables 1 and 2 present the results of stable carbon isotope measurements for low-molecular-weight dicarboxylic acids

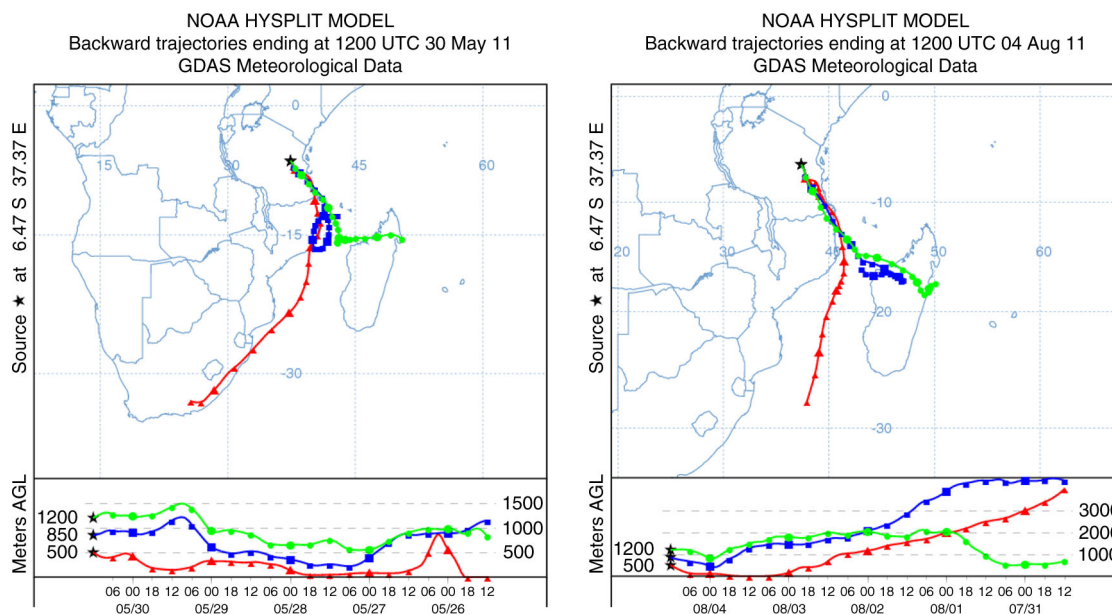


Fig. 2. Typical examples of 5-d backward air mass trajectories arriving at Morogoro during May to August 2011 sampling period.

Table 1. Stable carbon isotope ratios ($\delta^{13}\text{C}$, ‰) of dicarboxylic acids, glyoxylic acid and glyoxal in $\text{PM}_{2.5}$ aerosols collected from Tanzania, in July and August 2011

Date	Sample ID	Dicarboxylic acids				Glyoxylic acid ωC_2	Glyoxal Gly
		Oxalic C_2	Malonic C_3	Succinic C_4	Phthalic Ph		
28/7	TAN01	−20.2	−18.7	−23.4	NA	NA	NA
29/7	TAN02	−15.9	−20.9	−20.6	−27.1	−29.5	−25.4
1/8	TAN03	−18.3	−18.8	−21.8	NA	−21.4	−19.9
2/8	TAN04	−18.1	−20.7	−22.5	NA	−22.6	−18.3
3/8	TAN05	−17.0	−18.9	−20.9	NA	−18.3	NA
4/8	TAN06	−16.9	−20.4	−16.8	−28.7	−24.0	−15.4
5/8	TAN07	−21.3	−18.8	−22.3	−28.2	−24.0	−25.6
6/8	TAN08	NA	−20.8	NA	NA	−24.0	NA
7/8	TAN09	−17.9	−18.8	−23.7	NA	−23.7	−19.2
8/8	TAN10	−18.6	−19.6	−24.0	NA	−17.6	−17.3
	Mean	−18.3	−19.6	−21.8	−27.5	−22.5	−20.2
	±SD	1.7	1.0	2.2	0.8	3.5	3.9

Analytical errors for $\delta^{13}\text{C}$ are within 0.2‰.

NA: Not available.

(C_2 , C_3 , C_4 , C_9), phthalic acid (Ph), glyoxylic acid (ωC_2) and glyoxal (Gly) in $\text{PM}_{2.5}$ and PM_{10} aerosols, respectively. $\delta^{13}\text{C}$ of dominant diacids (C_2 , C_3 and C_4) ranged from −15.9 to −24.0‰ in $\text{PM}_{2.5}$ with mean of −18.3‰, −19.6‰ and −21.8‰, respectively, whereas those in PM_{10} ranged from −15.7 to −32.2‰ with mean of −19.9‰, −20.2‰ and −23.3‰, respectively. The mean $\delta^{13}\text{C}$ of glyoxylic acid (ωC_2) (−22.5‰) and glyoxal (−20.2‰) in $\text{PM}_{2.5}$ are larger than those (−26.7‰ and −23.7‰) of PM_{10} by about 4‰ and 2‰, respectively.

Table 2. Stable carbon isotope ratios ($\delta^{13}\text{C}$, ‰) of dicarboxylic acids, glyoxylic acid and glyoxal in PM_{10} aerosols collected from Tanzania, in May through August 2011

Date	Sample ID	Dicarboxylic acids					Glyoxylic acid ωC_2	Glyoxal Gly
		Oxalic C_2	Malonic C_3	Succinic C_4	Azelaic C_9	Phthalic Ph		
30/5	TAN11	−20.9	−21.9	−27.8		NA	−25.9	−30.5
31/5	TAN12	−23.3	−23.8	−21.5		NA	−29.3	−27.1
1/6	TAN13	−18.2	−20.8	NA		−21.5	−18.2	−23.3
2/6	TAN14	−18.1	−21.8	−19.8		NA	−25.3	NA
4/6	TAN15	−19.8	−18.8	−24.8		−22.7	−29.7	−23.9
5/6	TAN16	−17.3	−18.6	−21.3		NA	−33.0	NA
6/6	TAN17	−15.7	−18.5	−23.6		NA	−27	−30.6
7/6	TAN18	−24.5	−19.5	−21.2		NA	−35.4	−27.8
9/6	TAN19	−23.1	−21.7	−23.9		NA	−22.8	−18.8
12/6	TAN20	−20.1	−19.2	−22.6		NA	−31.1	NA
28/7	TAN21	−19.5	−19.0	−21.4	−29.8	−24.2	−23.5	−17.9
29/7	TAN22	−16.2	−18.5	−26.1	NA	NA	−18.8	NA
1/8	TAN23	−17.3	−17.4	−20.2	−26.7	−25.4	−24.5	−20.2
2/8	TAN24	−17.6	−20.5	−23.4	−26.3	NA	−21.6	−21.1
3/8	TAN25	−26.4	−29.0	−32.2	−33.4	−30.5	−31.6	−29.0
4/8	TAN26	−18.8	−19.3	−21.4	−26.3	−25.3	−24.4	−15.8
5/8	TAN27	−21.5	−20.9	−24.4	NA	NA	−26.9	−20.6
6/8	TAN28	−18.3	−18.9	−25.8	NA	NA	−26.3	−24.8
7/8	TAN29	−24.3	−18.8	−23.5	NA	NA	−36.5	NA
8/8	TAN30	−16.2	−17.1	−18.5	NA	−26.7	−21.3	NA
	Mean	−19.9±	−20.2	−23.3	−28.5	−25.2	−26.7	−23.7
	±SD	3.1	2.7	3.2	3.1	2.9	5.1	4.8

Analytical errors for $\delta^{13}\text{C}$ are within 0.2‰.

NA: Not available.

(Tables 1 and 2). Oxalic acid and Gly in $PM_{2.5}$ showed similar trend of $\delta^{13}C$ values in the samples during the campaign, suggesting that photochemical pathways for the formation of the acid and aldehyde are similar. Glyoxylic acid and Gly are reported as important precursors of oxalic acid via the oxidation of aromatic hydrocarbons and isoprene (Ervens et al., 2004; Lim et al., 2005).

On the other hand, C_9 was abundantly observed in the aerosol samples collected in July to August. Its $\delta^{13}C$ values (mean: -28.5‰) for PM_{10} are more depleted in ^{13}C compared to C_2 – C_4 diacids. The $\delta^{13}C$ signature of C_9 diacid suggests that the contributions of tropical organic emissions from C_3 plant are more significant than those of C_4 plant. Unfortunately, the $\delta^{13}C$ measurements of C_9 in $PM_{2.5}$ samples were not available due to the lower concentrations. C_9 diacid is mainly produced by atmospheric oxidation of unsaturated fatty acids that are emitted from either terrestrial or marine biological sources (Kawamura et al., 1996, 2000) and/or biomass burning (Kawamura et al., 1996). The smaller $\delta^{13}C$ signature of C_9 suggests that its major sources (unsaturated fatty acids) are terrestrial higher plants, not marine plankton, because terrestrial organic materials are more depleted in ^{13}C compared to marine organic materials (Fang et al., 2002).

Phthalic acid (Ph) showed smaller $\delta^{13}C$ values (mean: -27.5‰) than those of C_2 – C_4 diacids, ωC_2 and Gly. The observed ^{13}C depletion of Ph in both $PM_{2.5}$ and PM_{10} suggest an anthropogenic contribution from combustion sources (Kawamura and Kaplan, 1987) and/or atmospheric photochemical degradation of polycyclic aromatic hydrocarbons such as naphthalene (Kawamura and Ikushima, 1993). Open burning of municipal solid waste (large amounts of plastics) is very common in Tanzania (Kassim,

2006), together with local anthropogenic emissions. These sources should also be responsible for the aromatic diacid (Yassaa et al., 2001; Simoneit et al., 2005; Kawamura and Pavuluri, 2010).

The box plot in Fig. 3 shows statistical distributions of $\delta^{13}C$ of diacids, glyoxylic acid and glyoxal in $PM_{2.5}$ and PM_{10} . We found a decreasing trend in $\delta^{13}C$ for C_2 to C_4 diacids in $PM_{2.5}$ with C_2 diacid being slightly more enriched in ^{13}C than C_3 and C_4 diacids (Table 1 and Fig. 3). The less negative $\delta^{13}C$ of lower carbon number diacids can be explained by the isotopic fractionations that may occur during breakdown of diacids, e.g. iron-oxalate complex and, to a lesser extent, iron-malonate complex (Kawamura et al., 2012). Oxalic acid and Ph in both $PM_{2.5}$ and PM_{10} show the largest and smallest median $\delta^{13}C$ values, respectively. $\delta^{13}C$ of glyoxylic acid (ωC_2) and Gly showed fairly high values in $PM_{2.5}$, but they are significantly lower than that of C_2 diacid in PM_{10} (Fig. 3b). Although oxalic acid (most enriched with ^{13}C) has been proposed as an end product of the atmospheric oxidation of longer-chain diacids and other precursors such as ωC_2 and Gly (Kawamura et al., 1996; Sempéré and Kawamura, 2003), this study suggests that even C_2 can be decomposed in the atmosphere.

The range and average of $\delta^{13}C$ for C_2 , C_3 and C_4 diacids in aerosols from Morogoro, Tanzania (Tables 1 and 2), are comparable to those reported for tropical aerosols from Chennai, India (range: -9.2‰ to -27.4‰ , ave.: -17.1‰ , -20.8‰ and -22.5‰ , respectively) (Pavuluri et al., 2011) and for suburban aerosols from Sapporo, Japan (range: -14.0‰ to -25.3‰ , ave.: -18.8‰ , -21.7‰ and -22.7‰ , respectively) (Aggarwal and Kawamura, 2008). It is likely that C_2 and, to a lesser extent, C_3 are

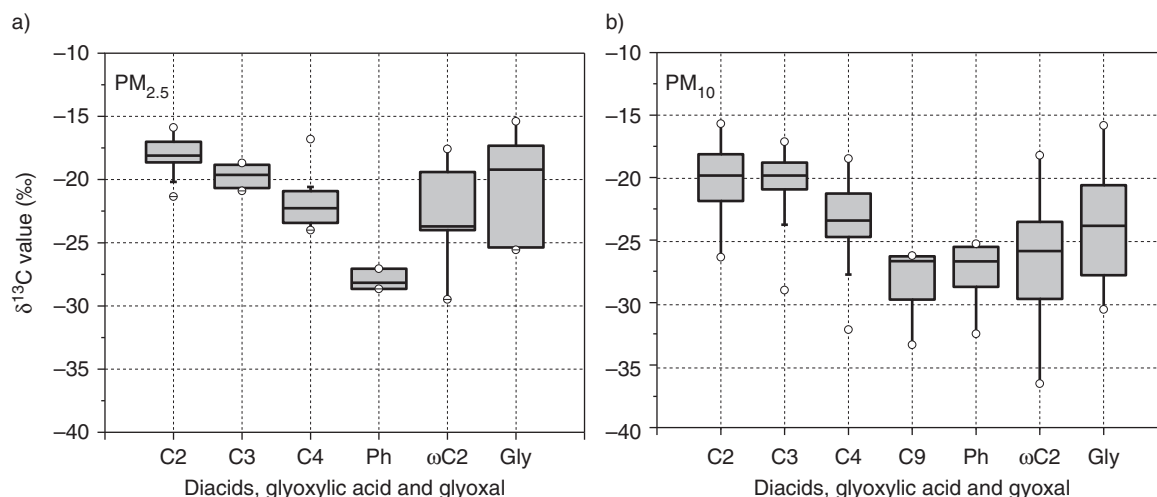


Fig. 3. Box plot of stable carbon isotope ratios of diacids, glyoxylic acid (ωC_2) and glyoxal (Gly) in $PM_{2.5}$ and PM_{10} aerosols from Morogoro, Tanzania, collected during the campaign. Each box shows the median (black line), the interquartile range (box) and the minimum and maximum values. Open circles show the outliers.

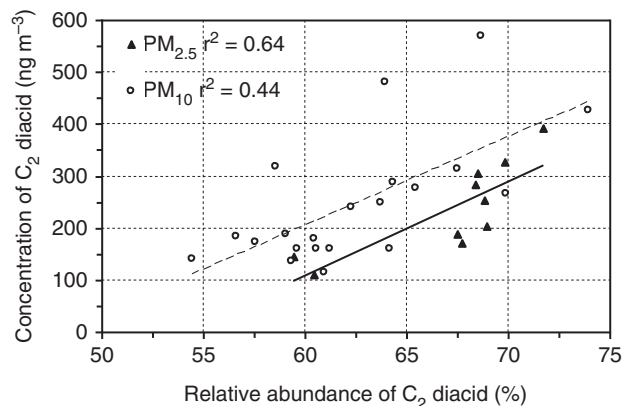


Fig. 4. Relation between concentrations of oxalic (C_2) acid and its relative abundance to total diacids in $PM_{2.5}$ and PM_{10} during 2011 sampling period in Morogoro, Tanzania. Data from Mkoma and Kawamura (2013).

photochemically aged during long-range atmospheric transport. The larger $\delta^{13}C$ values of lower molecular weight diacids in particular C_2 (Fig. 3a and b) indicate that the aerosols in Morogoro have significantly been subjected to photochemical processing in the tropical atmosphere during long-range transport from continental source regions in Tanzania, Mozambique and Madagascar (Fig. 2).

3.2. Relation of $\delta^{13}C$ to relative abundance of oxalic acid

The relative abundance of C_2 diacid ($C_2\%$) to total diacids has been proposed as a measure of photochemical processing (Kawamura and Sakaguchi, 1999). Concentrations of C_2 positively correlated with $C_2\%$ in the $PM_{2.5}$

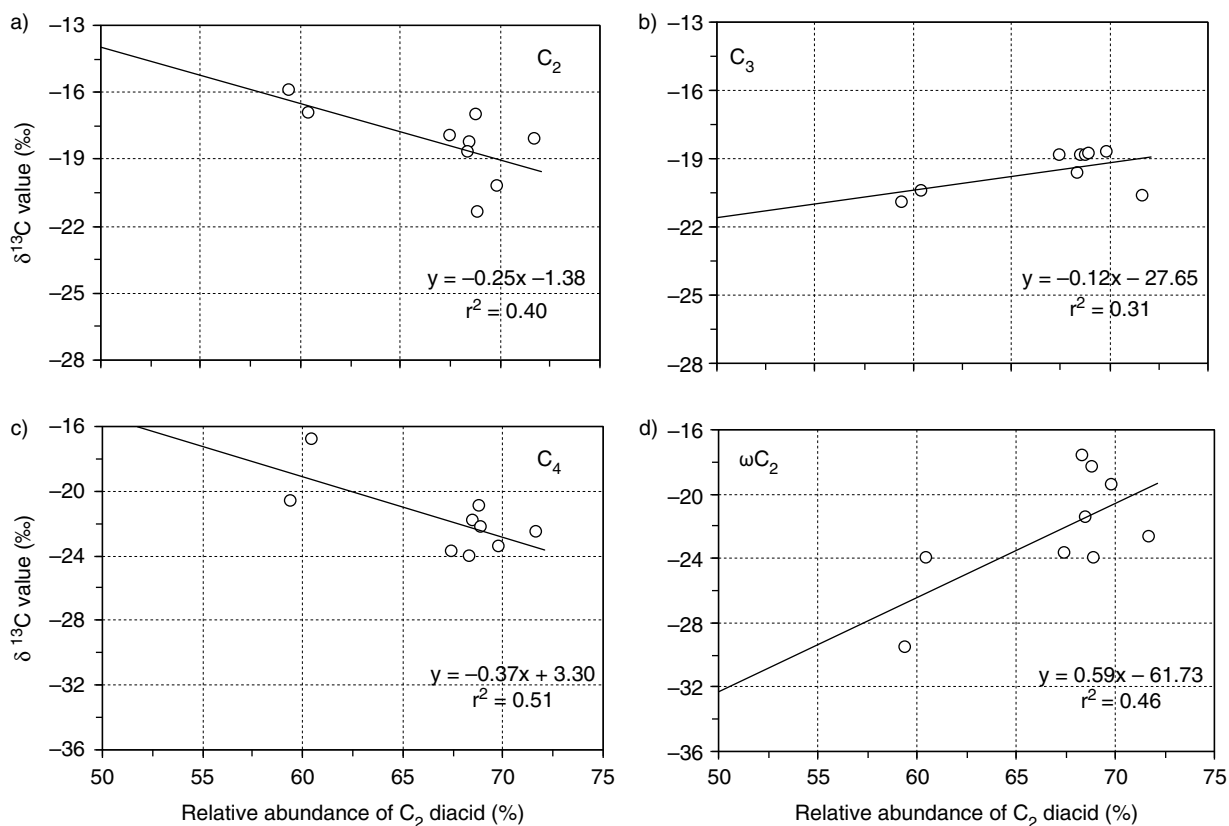


Fig. 5. Plot showing the linear relation of stable carbon isotopic composition ($\delta^{13}C$) for (a) C_2 , (b) C_3 , (c) C_4 and (d) ωC_2 acids with relative abundance of oxalic acid ($C_2\%$) to total diacids in $PM_{2.5}$ during 2011 sampling campaign in Morogoro, Tanzania.

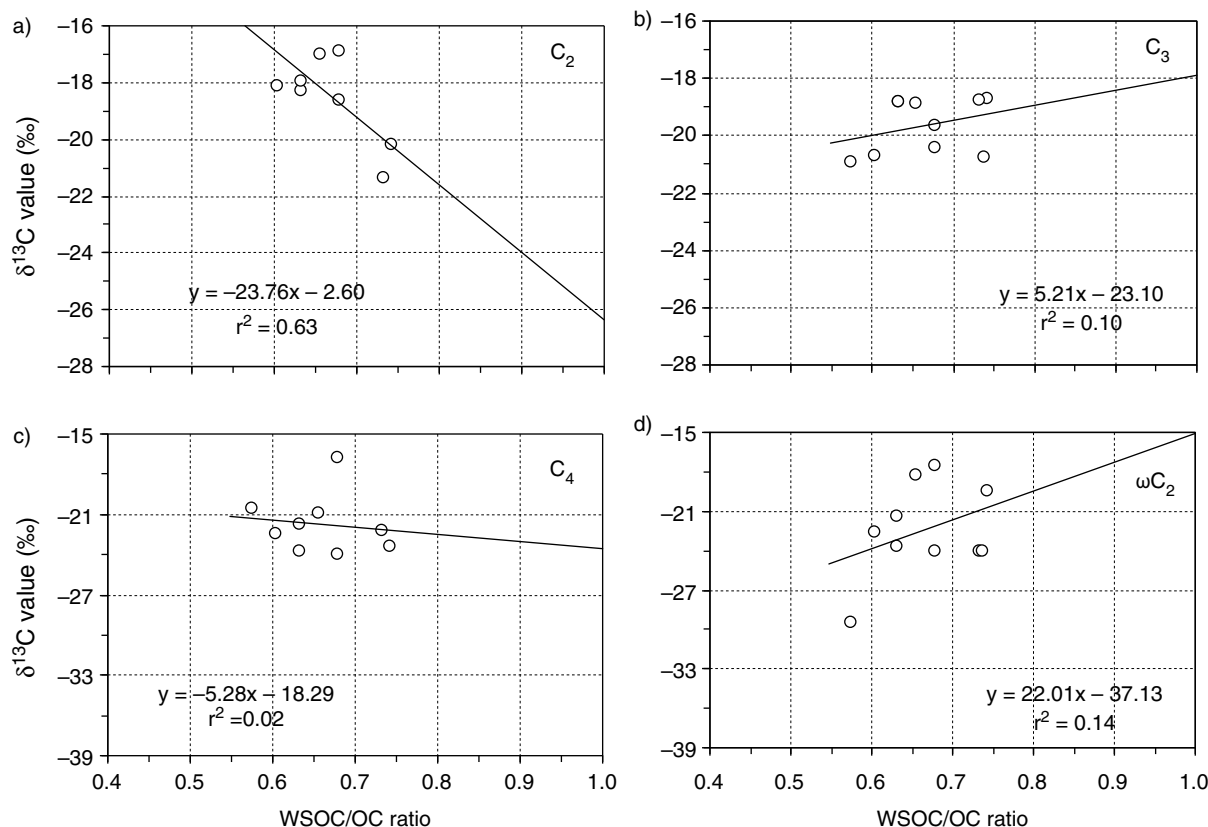


Fig. 6. Relation between stable carbon isotope ratios ($\delta^{13}\text{C}$ value) of diacids and WSOC/OC ratio in $\text{PM}_{2.5}$ during 2011 sampling period in Morogoro, Tanzania.

and PM_{10} aerosols from Morogoro (Fig. 4), indicating that preferential production of C_2 is associated with photochemical processing of organic aerosols in the atmosphere, being similar to that reported in tropical aerosols from Chennai, India (Pavuluri et al., 2011). The air mass trajectories suggested that the air masses are mixed with fresh precursors along the transport pathway as they passed over the continent (Fig. 2) where the biomass/biofuel burning emissions are significant.

Figure 5 shows $\delta^{13}\text{C}$ of C_2 , C_3 , C_4 diacids and ωC_2 as a function of relative abundance of oxalic acid ($\text{C}_2\%$) to total diacids in $\text{PM}_{2.5}$. The $\delta^{13}\text{C}$ of C_2 negatively correlate with $\text{C}_2\%$ (Fig. 5a) whereas those of C_3 positively (although weak) correlate with $\text{C}_2\%$ (Fig. 5b). Similar trend was obtained for C_4 diacid (Fig. 5c), suggesting an enrichment of ^{13}C in C_4 as well. However, the $\delta^{13}\text{C}$ of ωC_2 did show a positive correlation with $\text{C}_2\%$, suggesting that photochemical decomposition of ωC_2 is one of key factors responsible for the increase of $\delta^{13}\text{C}$ (Kawamura et al., 2012). On the other hand, PM_{10} samples did not show any significant correlations, except for C_4 diacid, which negatively correlated with $\text{C}_2\%$ ($r^2 = 0.38$). These results may suggest that the isotopic enrichment of the remaining small organic acids occur in fine particles ($\text{PM}_{2.5}$). The observed $\delta^{13}\text{C}$

values for diacids in aerosols from Morogoro suggest that some organics (e.g. C_3) were photochemically less aged (fresh), although average ambient temperatures ($> 25^\circ\text{C}$) and solar radiations were relatively high during the sampling periods.

3.3. $\delta^{13}\text{C}$ of diacids, glyoxylic acid and glyoxal and photochemical processes

Atmospheric photochemical reactions, evaporation and isotope exchange with OC could contribute to the systematic differences in the isotopic composition of dicarboxylic acids (Anderson et al., 2004; Irei et al., 2006). However, under the ambient temperature and pressure, evaporation-related isotopic fractionations and isotope exchange between OC species and diacids are insignificant (Wang and Kawamura, 2006). Shorter-chain diacids can be formed by the photochemical breakdown of longer-chain diacids (Kawamura and Sakaguchi, 1999) and other precursors. The increasing trends of $\delta^{13}\text{C}$ values for saturated diacids with a decrease in carbon numbers could be explained mainly by the kinetic isotope effect for the photochemical degradation of iron-oxalate/malonate complex (Wang and

Kawamura, 2006; Kawamura et al., 2012). On the other hand, a laboratory study has provided an evidence for the isotopic enrichment of ^{13}C in the remaining oxalic acid with photochemical aging; this approach is useful for better interpretation of atmospheric isotope measurements in terms of the extent of atmospheric processing of aerosols (Kawamura et al., 2012).

The ratio of WSOC/OC is a measure of photochemical processing or aging during atmospheric transport (Yang et al., 2004; Aggarwal and Kawamura, 2008), because prolonged photochemical oxidation of organics results in secondary organic aerosol (SOA) enriched with polar and thus water-soluble compounds. Figure 6 presents relations of the isotopic composition of diacids with WSOC/OC ratios in $\text{PM}_{2.5}$. Interestingly, oxalic acid (C_2) showed a negative correlation with WSOC/OC ratio whereas C_3 and ωC_2 showed a positive correlation (Fig. 6). Meanwhile, C_4 showed no correlation. However, such a trend was not observed for PM_{10} , except for C_4 diacid that showed a negative correlation with WSOC/OC ratio ($r^2 = 0.14$). The negative correlation between the isotopic composition of C_2 and WSOC/OC ratios supports that photochemical breakdown of C_2 would increase $\delta^{13}\text{C}$ of the remaining C_2 . C_2 is one of the important contributors to WSOC.

4. Conclusions

In this study, we determined for the first time stable carbon isotope ratios of diacids, glyoxylic acid and glyoxal in $\text{PM}_{2.5}$ and PM_{10} tropical aerosol samples that were collected between May and August 2011 in Tanzania (East Africa). Oxalic acid (C_2) showed larger $\delta^{13}\text{C}$ values than other species, suggesting photochemical processing of water-soluble organic aerosols. A slight decrease of $\delta^{13}\text{C}$ was observed with an increase in carbon numbers from C_2 to C_4 diacids in $\text{PM}_{2.5}$. Higher $\delta^{13}\text{C}$ values of C_2 and C_3 diacids and Gly in $\text{PM}_{2.5}$ and $\text{C}_2\text{--C}_3$ diacids in PM_{10} were found whereas C_9 and Ph were depleted with ^{13}C in both fractions. These observations suggest that the higher $\delta^{13}\text{C}$ of $\text{C}_2\text{--C}_3$ diacids compared to C_4 diacid may be associated with kinetic isotope effects for photochemical degradation of diacids and related compounds. Although the initial $\delta^{13}\text{C}$ value of diacids can depend on their original (precursor) sources, enrichment of ^{13}C caused by aerosol aging is more important in fine particles to control the stable carbon isotopic composition of lower molecular weight diacids in the ambient atmosphere.

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