Atmos. Chem. Phys. Discuss., 12, 25657–25701, 2012
www.atmos-chem-phys-discuss.net/12/25657/2012/
doi:10.5194/acpd-12-25657-2012
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Atmospheric Chemistry and Physics Discussions

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

Size distributions of dicarboxylic acids, ketocarboxylic acids, α-dicarbonyls and fatty acids in atmospheric aerosols from Tanzania, East Africa during wet and dry seasons

S. L. Mkoma[1,2] **and K. Kawamura**[1]

[1]Institute of Low Temperature Science, Hokkaido University, N19 W08, Kita-ku, Sapporo 060-0819, Japan
[2]Department of Physical Sciences, Faculty of Science, Sokoine University of Agriculture, P.O. Box 3038, Chuo Kikuu, Morogoro, Tanzania

Received: 21 August 2012 – Accepted: 6 September 2012 – Published: 27 September 2012

Correspondence to: S. L. Mkoma (stelyusm@gmail.com)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Atmospheric aerosol samples of $PM_{2.5}$ and PM_{10} were collected during the wet and dry seasons in 2011 from a rural site in Tanzania and analysed for water-soluble dicarboxylic acids, ketocarboxylic acids, α-dicarbonyls and fatty acids using a gas chromatography (GC) and GC/mass spectrometry. Here we report the size distribution and sources of diacids and related compounds for wet and dry seasons. 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 ketoacids and α-dicarbonyls, respectively in both seasons in $PM_{2.5}$ and PM_{10}. Mean concentration of C_2 in $PM_{2.5}$ ($121.5 \pm 46.6\,ng\,m^{-3}$) was lower in wet season than dry season ($258.1 \pm 69.5\,ng\,m^{-3}$). Similarly, PM_{10} samples showed lower concentration of C_2 ($168.6 \pm 42.4\,ng\,m^{-3}$) in wet season than dry season ($292.4 \pm 164.8\,ng\,m^{-3}$). Relative abundances of C_2 in total diacids were 65.4 % and 67.1 % in $PM_{2.5}$ and 64.6 % and 63.9 % in PM_{10} in the wet and dry seasons, respectively. Total concentrations of diacids (289–362 m^{-3}), ketoacids (37.8–53.7 $ng\,m^{-3}$), and α-dicarbonyls (5.7–7.8 $ng\,m^{-3}$) in Tanzania are higher to those reported at a rural background site in Nylsvley (South Africa) but comparable or lower to those reported from sites in Asia and Europe. Diacids and ketoacids were found to be present mainly in the fine fraction in both seasons (total α-dicarbonyls in the dry season), suggesting a production of organic aerosols from pyrogenic sources and photochemical oxidations. The averaged contributions of total diacid carbon to aerosol total carbon were 1.4 % in $PM_{2.5}$ and 2.1 % in PM_{10} in wet season and 3.3 % in $PM_{2.5}$ and 3.9 % in PM_{10} in dry season whereas those to water-soluble organic carbon were 2.2 % and 4.7 % in $PM_{2.5}$ and 3.1 % and 5.8 % in PM_{10} during the wet and dry seasons, respectively. These ratios suggest an enhanced photochemical oxidation of organic precursors and heterogeneous reactions on aerosols under strong solar radiation and high humidity. Correlations among organic components and relations between source tracers with diacids and related compounds in both seasons

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showed influence of mixed sources from natural biogenic emissions, biomass burning, biofuel combustion, and enhanced photochemical production.

1 Introduction

Low molecular weight dicarboxylic acids, ketoacids and α-dicarbonyls are important components that contribute to water-soluble organic carbon (WSOC) in aerosol particles (Simoneit et al., 2004; Wang et al., 2006b). Dicarboxylic acids and related compounds have been reported to influence human health (Highwood and Kinnersley, 2006), hygroscopic property of aerosols (McFiggans et al., 2005), and contribute to the cloud condensation nuclei (CCN) activity (Gierlus et al., 2012). Changes in chemical composition and CCN activity can alter the optical properties of aerosol particles (Reid et al., 1998) and affects cloud microphysical properties and hence precipitation patterns and cloud albedo (Reid et al., 1998; Ramanathan et al., 2001).

Dicarboxylic acids and related compounds are derived from primary sources and secondarily produced from different precursor species via photochemical reactions. Biomass burning (Gao et al., 2003; Falkovich et al., 2005; Kundu et al., 2010a), fossil fuel combustions (Kawamura and Kaplan, 1987; Ho et al., 2006) are major primary sources. Photochemical-oxidation of biogenic unsaturated fatty acids (Kawamura and Gagosian, 1987), volatile organic compounds (VOCs) from biogenic and anthropogenic emissions, and aromatic hydrocarbons and cyclic olefins (Kawamura et al., 1996a) are important secondary sources. Atmospheric loadings of organic aerosols are significantly influenced by primary emissions from biomass burning and secondary productions (Claeys et al., 2004; Wang et al., 2006a; Carlton et al., 2006). Recently, emission of isoprene and other biogenic VOCs followed by the subsequent oxidation in the atmosphere has been proposed as an important source of oxalic acid (Myriokefalitakis et al., 2011).

In Tanzania, biomass/wood fuels accounts for major source of energy providing up to 90 % of the total national energy consumption and 8 % from petroleum products and

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2 % from electricity (URT, 2012). Burning of biofuels such as wood, charcoal, and agricultural waste is the main energy use in this country. Charcoal burning for cooking is very common not only in rural areas but also in cities. On the other hand, dumping of domestic and municipal solid waste into open landfills and the subsequent uncontrolled open burning are common in the country. Therefore, photochemical reactions together with anthropogenic biofuel combustion produce various organic species including dicarboxylic acids and related compounds to form atmospheric particles, reading to the deterioration of the air quality in Tanzania.

Studies have reported that dicarboxylic acids and related compounds are ubiquitously present in the atmospheric aerosols from various environments in continental rural and urban (Limbeck et al., 2001; Kerminen et al., 2000; Kawamura and Yasui, 2005; Limbeck et al., 2005; Ho et al., 2006; Hyder et al., 2012; Wang et al., 2012), coastal and remote marine (Kawamura and Sakaguchi, 1999; Mochida et al., 2007; Rinaldi et al., 2011), and polar sites (Kawamura et al., 1996b; Narukawa et al., 2003). However, little is known about tropical organic aerosols in Africa and no extensive studies have been conducted (Simoneit et al., 1988; Cachier et al., 1991, 1995; Limbeck and Puxbaum, 1999; Limbeck et al., 2001; Gao et al., 2003). Here we report for the first time the molecular composition of dicarboxylic acids, ketocarboxylic acids, α-dicarbonyls and fatty acids in aerosols from a rural background site in Tanzania, East Africa and discuss their size distributions, seasonal variations, sources and formation pathways.

2 Experimental

2.1 Site description

Aerosol sampling was carried out at a typical rural site in Morogoro (06°47′40.8″ S, 37°37′44.5″ E, altitude 504 m, a.s.l), located about 200 km west of the Indian Ocean, and the city of Dar es Salaam, a business capital in Tanzania. The site lies at the base

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of Uluguru Mountains, which rise to 2648 m a.s.l. and are characterised as residential area with small-scale agricultural fields (cereals crops), and cattle grazing fields. Like in most other developing countries where poverty is concentrated in rural areas, Tanzania with a population of 42.7 million people (July 2011, estimates) has 25 % of its population living below basic needs poverty line (2008 estimate). Therefore, their main sources of fuel for domestic cooking and heating are wood and charcoal.

2.2 Aerosol sampling

Aerosol samples of ($PM_{2.5}$ and PM_{10}) were collected using low volume samplers (Gent type, flow rate 17.0 l min^{-1}) in parallel (Maenhaut et al., 1994) in the 2011 wet and dry seasons. The samplers were placed at a fenced meteorological observatory located at Solomon Mahlangu campus of Sokoine University of Agriculture. Aerosol collection was performed approximately at 2.7 m a.g.l. using quartz fibres filters (Pallflex 2500QAT-UP, 47 mm) which were pre-baked at 450 °C for 4 h in a furnace to eliminate adsorbed organics before use. A total of 21 sets of actual samples and 2 field blanks were collected using each sampler on approximately 24 h basis (exchange of filters was done at 07:30 a.m.). Before and after sampling the filters were placed in a pre-heated glass vial with a Teflon-lined screw cap and kept frozen at −20 °C during storage. The samples were transported to the atmospheric chemistry laboratory at the Institute of Low Temperature Sciences (ILTS), Hokkaido University (Japan), where the samples were stored at −20 °C prior to analysis. All procedures were strictly quality-controlled to avoid any possible contamination of the samples.

2.3 Chemical analysis

Filter samples were analyzed for water-soluble dicarboxylic acids, ketocarboxylic acids, α-dicarbonyls and fatty acids using the method reported by Kawamura and Ikushima (1993). Briefly, a 1.54 cm^2 punch of each quartz fibre filter was extracted three times with 10 ml ultra pure organic-free water (resistivity of > 18.2 MΩcm) under

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ultrasonication for 10 min. To remove insoluble particles and filter debris, the extracts were passed through a glass column (Pasteur pipette) packed with quartz wool. The pH of the extracts were adjusted to 8.5–9.0 with 0.1 M KOH (potassium hydroxide) solution, concentrated almost to dryness using a rotary evaporator under vacuum and then derivatized to dibutyl ester (for carboxyl group) and dibutoxy acetals (for keto group) with 14 % boron trifluoride (BF_3)/n-butanol at 100 °C for 1 h. The derived esters and acetals were dissolved in n-hexane, washed with pure water three times and the extracts were again concentrated using rotary evaporator under vacuum. After nitrogen blow down to near dryness, n-hexane (100 µl) was added and the derivatives were analyzed using a capillary gas chromatography (GC; HP 6890). Peaks were identified by comparing GC retention time with authentic standards and confirmed by mass spectral examination using a gas chromatography/mass spectrometer (GC/MS).

Recovery experiments were performed by spiking authentic standards to a pre-combusted quartz fibre filter. The recoveries were 81 % to 88 % for oxalic acid and more than 92 % for malonic, succinic, glutaric, and adipic acids. Following the same analytical procedure in our laboratory, recoveries for glyoxylic acid, pyruvic acid and methylglyoxal were reported to be 88 %, 72 % and 47 %, respectively (Kawamura and Yasui, 2005). Reproducibility of filter sample was within 4 % for major species. GC chromatograms of field blanks showed small peaks for oxalic, malonic, phthalic, and glyoxylic acids, however, they were less than 1 % (oxalic acid), 3 % (malonic acid), 8 % (phthalic acid) and 5 % (glyoxylic acid) of real samples. Lower field blanks levels 0.66 % (oxalic acid) and 5.6 % (phthalic acid) of the aerosol samples were reported by Kawamura and Yasui (2005). All the reported concentrations of diacids and related compounds are corrected for the field blanks. Details for measurement of gravimetric aerosol mass and analyses of total carbon (TC), organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), levoglucosan and water-soluble inorganic ions are described elsewhere (Mkoma et al., 2012).

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2.4 Meteorology and air mass trajectories

Morogoro, where the sampling site locates, experiences a humid tropical savanna climate with warm wet season and cold dry season (TMA, 2011). The ambient temperature during the campaigns varied from 22.9 °C to 29.1 °C (average: 26 °C) in the wet season and 21.1–28.2 °C (average: 24.6 °C) in the dry season. The site is sensitive to frequent phenomenon of temperature inversion events due to its proximity to the foothill of the Uluguru Mountain ranges. The daily average relative humidity ranged from 65 % to 96 % (average: 81 %) in the morning hours and from 41 % to 60 % (average: 50 %) in the afternoon. In the wet season campaign (30 May to 13 June), there were only 4 days without rain. In contrast, there were only 2 rainy days in the dry season (28 July to 8 August). However, the entire sampling period was rather dry and few aerosol samples were met with a very weak rain. The prevailing winds during both campaigns were the southeasterly (SE) monsoons with daily average wind speed of 4.1 $m s^{-1}$ and 12 $m s^{-1}$ in the wet and dry seasons, respectively.

To find out the possible source regions of air masses at Morogoro during the campaigns, we computed 5-day backward air mass trajectories at an altitude of 500 m for every 24 h using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model from NOAA/ARL (http://ready.arl.noaa.gov/HYSPLIT.php; Draxler and Rolph, 2012). The trajectory sectors showed similar transport pathways and source regions in both wet and dry seasons (Fig. 1). The air masses that arrived in Morogoro were mainly from the Indian Ocean over continental in Madagascar, Mozambique or Tanzania.

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3 Results and Discussion

3.1 Size distributions and seasonal variations of diacids and related compounds

We determined diacids, ketoacids, α-dicarbonyls, and fatty acids during the wet and dry seasons in $PM_{2.5}$ and PM_{10} at a rural site in Tanzania (Table 1). The detected compounds were saturated straight chain diacids (C_2–C_9); unsaturated aliphatic (maleic, fumaric, and methylmaleic), brached chain (methylmalonic, iC_4 methylsuccinic, iC_5) and aromatic (phthalic, isophthalic, and terephthalic acids) diacids; ketocarboxylic acids (ωC_2–ωC_9 and pyruvic acid); α-dicarbonyls (glyoxal and methylglyoxal), and fatty acids (C_{14}, C_{16}, C_{18}, $C_{18:1}$, C_{20}, C_{22} and C_{24}). Longer-chain diacids (C_{10}–C_{12}) were below the detection limit (ca. 0.005 ng m^{-3}) in all the samples.

Size distributions and average molecular compositions of diacids, ketoacids, α-dicarbonyls and fatty acids in wet and dry seasons are shown in Figs. 2 and 3. Total concentrations of diacids ranged from 97.2–547.5 ng m^{-3} in $PM_{2.5}$ and 165.5–959.5 ng m^{-3} in PM_{10}. Oxalic acid (C_2) was the most abundant diacid followed by succinic (C_4) and/or malonic (C_3) acids in two seasons and sizes. Mean concentrations of C_2 in $PM_{2.5}$ were 121.5 ± 46.6 ng m^{-3} during the wet season and 258.1 ± 69.5 ng m^{-3} during the dry season whereas those in PM_{10} were 168.6 ± 42.4 ng m^{-3} 292.4 ± 164.8 ng m^{-3} during the wet and dry seasons (Table 1). The relative abundances of individual diacids to total saturated straight-chain (C_2–C_9) diacids in $PM_{2.5}$ and PM_{10} during the wet and dry seasons are shown in Fig. 4 as pie diagrams. The relative abundances of C_2 in total diacids were 65.4 % and 67.1 % in $PM_{2.5}$ and 64.6 % and 63.9 % in PM_{10} in the wet and dry seasons, respectively (Table 2 and Fig. 4). Higher relative abundances of oxalic acid in both seasons may suggest enhanced biomass burning activities (Narukawa et al., 1999), photochemical chain oxidations of precursors (Ervens et al., 2004) and ageing of organic aerosols during long-range atmospheric transport (Aggarwal and Kawamura, 2008) during the campaigns. Other studies reported

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the predominance of oxalic acid in aerosol samples from background sites in Africa (Limbeck and Puxbaum, 1999; Limbeck et al., 2001) and continental sites affected by biomass burning (Gao et al., 2003; Kundu et al., 2010a).

Concentrations of longer-chain diacids (C_6–C_9) varied in different seasons and size fractions with suberic acid (C_8) being the most abundant in the wet season in $PM_{2.5}$, C_6 and C_9 in the dry season in $PM_{2.5}$ and C_9 in both seasons in PM_{10}. As seen in Fig. 4, higher relative abundance of adipic acid (C_6) was found in the dry season in $PM_{2.5}$, suggesting its production by the oxidation of anthropogenic cyclohexene (Kawamura and Ikushima, 1993). Higher relative abundance of azelaic acid (C_9) in $PM_{2.5}$ during the dry season and in PM_{10} during both seasons suggests a photochemical oxidation of biogenic unsaturated fatty acids containing a double bond at carbon-9 position that are emitted from local vegetations (Kawamura and Gagosian, 1987). Phthalic acid (Ph) and terephthalic acid (t-Ph) had high abundances in $PM_{2.5}$ during the wet season and in PM_{10} during the dry season. The observed high abundances of these aromatic diacids suggest anthropogenic effect from combustion sources (Kawamura and Kaplan, 1987) and/or atmospheric photochemical degradation of polycyclic aromatic hydrocarbons such as naphthalene (Kawamura and Ikushima, 1993). In Tanzania, dumping of municipal solid waste (large amounts of plastics) into open landfills is very common and 60 % of daily domestic solid waste are disposed and subjected to open burning (Kassim, 2006). Plastic burning under open-fire conditions and local anthropogenic emissions in both seasons should be responsible for these aromatic acids (Yassaa et al., 2001; Simoneit et al., 2005; Kawamura and Pavuluri, 2011).

Mean concentrations of total ketoacids were $31.4 \pm 17.8\,ng\,m^{-3}$ and $59.6 \pm 19.3\,ng\,m^{-3}$ in $PM_{2.5}$ and $44.4 \pm 28\,ng\,m^{-3}$ and $78.3 \pm 44.9\,ng\,m^{-3}$ in PM_{10} during the wet and dry seasons, respectively (Table 1). Higher concentrations for ketoacids were found in the dry season in both sizes, suggesting an additional emission of volatile biogenic precursors from local vegetations. Glyoxylic acid (ωC_2), an important precursor of oxalic acid (Warneck, 2003), was the most abundant ketoacid in both seasons and sizes followed by 9-oxononoic acid (ωC_9). Interestingly, ωC_9 is mostly present in larger size (PM_{10})

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in both seasons (Table 1), suggesting that the production of ωC_9 via the oxidation of biogenic unsaturated fatty acids (Kawamura and Gagosian, 1987) occurs mainly in aerosol phase. This is in contrast to ωC_2, which is mostly present in fine fraction ($PM_{2.5}$) as seen in Table 1 and is mainly produced in gaseous phase. Other studies in China (Ho et al., 2007), India (Pavuluri et al., 2010), Japan (Aggarwal and Kawamura, 2008), Korea (Kundu et al., 2010b), Mongolia (Jung et al., 2010), and polar region (Kawamura et al., 2010) have reported predominance of ωC_2 in ketoacids.

Mean concentrations of total α-dicarbonyls in $PM_{2.5}$ were $6.4 \pm 3.0\,ng\,m^{-3}$ in wet season and $4.4 \pm 1.7\,ng\,m^{-3}$ in dry season whereas those in PM_{10} were $7.3 \pm 1.9\,ng\,m^{-3}$ and $8.0 \pm 3.5\,ng\,m^{-3}$ in the wet and dry seasons, respectively (Table 1). In both seasons and size fractions, glyoxal (Gly) was more abundant than methylglyoxal (Table 2). In contrast to diacids and ketoacids, higher concentrations of α-dicarbonyls were found in the wet season (higher temperature), indicating possibly enhanced photochemical production of α-dicarbonyls. The aldehyde group in dicarbonyls is highly susceptible for nucleophilic addition of oxygen forming carboxylic acid (Ervens et al., 2004; Fick et al., 2004).

Homologous series of straight chain fatty acids ($C_{14:0}$–$C_{24:0}$) and unsaturated fatty acid ($C_{18:1}$) were detected (Table 1). Mean concentrations of total fatty acids in $PM_{2.5}$ were $26.1 \pm 19.3\,ng\,m^{-3}$ and $31.9 \pm 15.4\,ng\,m^{-3}$ during the wet and dry seasons, respectively, whereas those in PM_{10} were $102 \pm 43.8\,ng\,m^{-3}$ and $117.2 \pm 72.4\,ng\,m^{-3}$. Average molecular compositions of fatty acids and their size distributions in the wet and dry seasons are shown in Figs. 2 and 3. Fatty acids with even carbon-number predominance were detected with the maximum of myristic acid ($C_{14:0}$) in $PM_{2.5}$ and palmitic acid ($C_{16:0}$) in PM_{10} in both seasons, indicating a significant emission of lipids from biological sources (Lechevalier, 1977; Simoneit, 1989). Palmitic acid ($C_{16:0}$) and stearic ($C_{18:0}$) showed higher concentrations in wet season in both sizes probably due to enhanced emissions from vegetation sources. In contrast, longer-chain fatty acids, behenic (C_{22}) and lignoceric (C_{24}), which are specific to terrestrial higher plants (Kawamura et al., 2003), were not detected in fine mode ($PM_{2.5}$), but were abundantly detected in coarse

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mode (PM_{10}). They showed higher concentrations of these species during the dry season, suggesting a long-range atmospheric transport of lipid compounds.

Higher concentration of azelaic acid (C_9) and higher ratios of C_9 to oleic acid ($C_{18:1}$) were found in the dry season for both sizes, suggesting that secondary formation of C_9 is significant during long-range atmospheric transport. Mean $C_9/C_{18:1}$ ratios in $PM_{2.5}$ were 0.63 and 4.5 and those in PM_{10} were 1.5 and 8.6 in the wet and dry seasons, respectively. Oxidation of $C_{18:1}$ (Kawamura and Gagosian, 1987; Stephanou and Stratigakis, 1993) is likely in the atmosphere to result in C_9 (through its precursor ωC_9) during the long-range transport. The lowest $C_9/C_{18:1}$ ratio in the wet season for $PM_{2.5}$ and PM_{10} may be due to enhanced emission of $C_{18:1}$ from surface waters in the Indian Ocean. Unsaturated fatty acids are enriched in sea surface microlayer and emitted to the marine atmosphere. On other hand, mean $C_{18:1}/C_{18:0}$ ratios in $PM_{2.5}$ were 1.2 and 1.9 in the wet and dry seasons, respectively whereas those in PM_{10} were 1.1 and 1.6, respectively. We found lower mean $C_{18:1}/C_{18:0}$ ratios in the wet season in both sizes, further suggesting enhanced photochemical degradation of $C_{18:1}$ under wet conditions during long-range atmospheric transport.

3.2 Temporal variations of diacids and related compounds

Figure 5a–e shows temporal variations of total aerosol mass, diacids, ketoacids, α-dicarbonyls and fatty acids in $PM_{2.5}$ and PM_{10} during the wet and dry seasons. Temporal variations of individual diacids (C_2–C_9) and Ph are given in Fig. 6a–f. Concentrations of C_2, C_3 and C_4 diacids showed similar temporal variations with higher concentrations during dry season in both sizes (Fig. 6a–c), suggesting more production and/or accumulation of the diacids in the dry season. The C_2/total diacids ratios in $PM_{2.5}$ were 0.65 ± 0.06 (range: 0.49–0.72) in wet season and 0.67 ± 0.04 (range: 0.59–0.72) in dry season whereas those in PM_{10} were 0.65 ± 0.05 (range: 0.59–0.76) in wet season and 0.64 ± 0.04 (range: 0.54–0.69) in dry season. Conversely, C_6 appears to increase from wet to dry season (Fig. 6d) whereas C_9 showed higher concentrations in $PM_{2.5}$ during the dry season (Fig. 6e). This suggests that there is more photochemical production

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of C_6 and C_9 in the dry season due to increased emissions of their precursors (i.e. unsaturated fatty acids) under strong radiation and high temperature. Concentrations of Ph were rather constant in two seasons in $PM_{2.5}$ whereas showed maximum concentrations in the dry season in PM_{10} (Fig. 6f).

3.3 Fine ($PM_{2.5}$) to coarse (PM_{10}) ratios

Mean $PM_{2.5}/PM_{10}$ ratios for total diacids, ketoacids, α-dicarbonyls and fatty acids in aerosol samples are shown in Fig. 7 for the wet and dry seasons. The ratios were calculated on the basis of the data for fine ($PM_{2.5}$) and coarse (PM_{10}) samples taken in parallel and averaged over all samples from the campaign. The results indicate that total diacids, ketoacids and α-dicarbonyls were mostly present in the fine fraction in both seasons (except for α-dicarbonyls in the dry season). This suggests a larger contribution of pyrogenically and photochemically produced organic aerosols, which are most likely enriched in fine particles. Contribution from primary biogenic emissions and soil dust, mostly associated with coarse particles could be significant source for α-dicarbonyls in the dry season. Strong correlation ($r^2 = 0.81$) was found between Ca^{2+} (crustal tracer) with the PM_{10} mass in the dry season (in contrast $r^2 = 0.17$ in the wet season). Mean $PM_{2.5}$ to PM_{10} ratios for total diacids and related compound are mainly larger than 60 % and larger ratios above 80 % were obtained for total diacids and total ketoacids in the dry season and total α-dicarbonyls in the wet season (Fig. 7). Other studies have reported association of diacids and related compounds with the fine ($PM_{2.5}$) fraction (Narukawa et al., 2003; Kawamura et al., 2007; Wang et al., 2012). Interestingly α-dicarbonyls showed a significantly high $PM_{2.5}/PM_{10}$ ratio (ca. 85 %) in wet season. Because glyoxal and methylglyoxal that are mostly present as gas in the atmosphere can form hydrated forms in the presence of moisture, it is reasonable that α-dicarbonyls are detected as fine particles during wet season.

In contrast, fatty acids were found mostly in the coarse particles in both seasons (Fig. 7). Fatty acids with carbon number > 14, in particular C_{16} are known to be mostly in particulate phase (Cheng et al., 2004), they are likely associated with coarse fraction.

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This suggests that fatty acids at our site are from mixed sources (Alfarra et al., 2004) and produced from primary sources such as viable microbiota in the ambient particles, marine biological activity or terrestrial higher plants. Natural components of lipid fractions (higher plant waxes) from rural, urban and oceanic regions have been reported to have predominance of C_{16} acid (Simoneit et al., 1988; Limbeck and Puxbaum, 1999; Cheng et al., 2004).

3.4 Seasonal contributions of diacids, ketoacids, and α-dicarbonyls to the PM mass, TC, and WSOC

Temporal variations in the contributions of total diacids to the aerosol mass, total carbon (TC), and water-soluble organic carbon (WSOC) in $PM_{2.5}$ and PM_{10} during the wet and dry seasons are given in Fig. 8a–c. We generally found that the mean ratios are higher in the dry season than in the wet season for both size fractions. The mean contributions of total diacids to $PM_{2.5}$ mass were 0.65 % (range: 0.38–0.89 %) in the wet season and 1.04 % (range: 0.57–1.39 %) in the dry season whereas those to PM_{10} mass were 0.97 % (range: 0.50–1.52 %) in the wet season and 1.20 % (range: 0.59–2.47 %) in the dry season. Total diacid-C/TC ratios ranged from 0.73 % to 5.0 % (mean: 2.4 ± 0.70 %) in $PM_{2.5}$ and 1.3 % to 3.2 % (mean: 3.0 ± 1.4 %) in PM_{10}. The averaged ratios of 1.4 % in $PM_{2.5}$ and 2.1 % in PM_{10} in the wet season are twice lower than 3.3 % in $PM_{2.5}$ and 3.9 % in PM_{10} in the dry season (Fig. 8b). The mean contributions of total diacids to TC at our site (2.4 % in $PM_{2.5}$ and 3.0 % in PM_{10}) are much higher than those reported in Sapporo (1.8 %) (Aggarwal and Kawamura, 2008) and in Tokyo (0.95 %) (Kawamura and Ikushima, 1993), in Chennai, India (1.6 %) (Pavuluri et al., 2010) and in Mongolia (0.60 %) (Jung et al., 2010). These comparisons suggest more enhanced photochemical production of diacids via gas-to-particle conversion of precursor organics in tropical Tanzania as well as heterogeneous reactions on aerosols under strong solar radiation and high humidity. However, the ratios at our site are lower than that (8.8 %) reported in remote marine aerosols including tropics (Kawamura and

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Sakaguchi, 1999), where photochemical processes are more enhanced during long-range atmospheric transport.

Contributions of total diacids to WSOC in $PM_{2.5}$ during the wet and dry seasons were 2.2 % (range: 1.1–3.0 %) and 4.7 % (range: 2.1–6.9 %), respectively, whereas those in PM_{10} were 3.1 % (range: 2.0–5.8 %) during the wet season and 5.8 % (range: 2.7–14.3 %) during the dry season. Higher ratios in the dry season further support enhanced photochemical oxidations of organic precursors and production of diacids, which are water-soluble, during the dry season. In fact the contributions of total diacids to WSOC in the dry season were 2 times higher than those for wet season in both sizes; 6.5 % and 14.4 % in $PM_{2.5}$ and 9.3 % and 17.4 % in PM_{10} for wet and dry seasons, respectively.

On the other hand, mean contributions of total ketoacids to TC in the wet and dry season were 0.29 % and 0.65 % in $PM_{2.5}$ and 0.54 % and 0.81 % in PM_{10}, respectively. Those ratios to WSOC were 0.43 % and 0.95 % in $PM_{2.5}$ and 0.86 % and 1.15 % in PM_{10}, respectively. Higher contributions of total ketoacids in the dry season suggest secondary production due to the oxidation of volatile and semivolatile organic precursors and photochemical aging of organic aerosols during long-range transport. In contrast, total α-dicarbonyls show similar contributions to TC (0.06 % and 0.05 % in $PM_{2.5}$ and 0.08 % and 0.09 % in PM_{10}) and to WSOC (0.09 % and 0.07 % in $PM_{2.5}$ and 0.11 % and 0.13 % in PM_{10}) during both seasons.

3.5 Comparison of molecular composition of diacids and related compounds with other studies

Table 3 shows mean concentrations of diacids, ketoacids, and α-dicarbonyls in Tanzania and those reported from other sites in Africa, Asia and Europe. Concentrations of total diacids in Morogoro (289–362 ng m^{-3}) are lower to those reported from Sapporo (390 ng m^{-3}), Tokyo (446 ng m^{-3}), Chennai (588 ng m^{-3}), Hong Kong (671 ng m^{-3}) and Jeju Island (648 ng m^{-3}) but comparable to that (359 ng m^{-3}) from Nainital and higher than those from Nylsvley (158.1 ng m^{-3}) and Salzburg (61.7 ng m^{-3}). Predominance of

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oxalic acid (C_2) found at our site is consistent with other studies (Table 3) except for Salzburg where malonic acid (C_3) was reported as the most abundant diacid. Oxalic acid is the end product of the photooxidation of aromatic hydrocarbons, isoprene, ethylene, and acetylene (Kawamura et al., 1996a; Lim et al., 2005) and may be emitted from biomass burning (Legrand and de Angelis, 1996; Kundu et al., 2010b). Concentrations of C_3 and C_4 are comparable to those from Nainital whereas those of C_6 and C_9 are comparable to those from Tokyo, Chennai and Hong Kong, but lower than those from Sapporo and Jeju Island. Adipic acid (C_6) and azelaic acid (C_9) are tracers for anthropogenic and biogenic emissions, respectively (Kawamura and Ikushima, 1993).

On the other hand, predominance of fumaric acid over maleic acid at our site, in contrast to literature values in Table 3 suggests that the Morogoro aerosols contain aged oxidation products of aromatic hydrocarbons emitted from regional pollution sources. Concentrations of phthalic (Ph) acid (mean: 12.9 ng m^{-3}), a tracer for vehicle emissions (Kawamura and Ikushima, 1993) are about 2 folds lower than that from Chennai (mean: 21 ng m^{-3}) and 7 folds lower than that from Hong Kong (mean: 83.9 ng m^{-3}). We found that concentration of t-Ph acid in $PM_{2.5}$ is similar to that reported from Sapporo (mean: 2.6 ng m^{-3}, Aggarwal and Kawamura, 2008) but is lower than those from Chennai (mean: 52 ng m^{-3}, Pavuluri et al., 2010) and Nainital (mean: 4.3 ng m^{-3}, Hegde and Kawamura, 2012). t-Ph could be produced from open burning of solid waste (plastic) (Simoneit et al., 2005; Kawamura and Pavuluri, 2010), which occurs commonly in Tanzania. Concentrations of total ketoacids in Morogoro (mean: 37.8–53.7 ng m^{-3}) with a predominance of ωC_2 are comparable to those from other sites whereas those of total α-dicarbonyls (mean: 5.7–7.8 ng m^{-3}) are lower than those reported in literature (Table 3).

We found higher abundances of C_4 than C_3 in $PM_{2.5}$ (and vice versa in PM_{10}), supporting the influence of biomass burning activities and atmospheric oxidation of diacids in $PM_{2.5}$. The C_3/C_4 ratio is used to understand the photochemical processes and atmospheric production of diacids in the atmosphere (Aggarwal and Kawamura, 2008; Kundu et al., 2010b). At Morogoro the average C_3/C_4 ratios were 0.72 and 0.81 in

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$PM_{2.5}$ and 1.3 and 1.0 in PM_{10} during the wet and dry seasons, respectively. These differences in the ratios are not significant, suggesting that higher temperature and solar radiation in tropics enhance the production of C_3 from photochemical oxidation of C_4 and other precursors in the atmosphere. When compared to literature values, our C_3/C_4 ratios are lower than those (1.5) reported in Tokyo (Kawamura and Ikushima, 1993) and 1.4 in Chennai (Pavuluri et al., 2010) but comparable to those (0.84) in Nainital (Hegde and Kawamura, 2012) and 1.3 in Jeju Island (Kawamura et al., 2004).

3.6 Source identification of diacids, ketoacids and α-dicarbonyls

Correlation matrix for diacids and related compounds in $PM_{2.5}$ and PM_{10} during the 2011 wet and dry seasons are given in Tables 4 and 5, respectively. Many combinations of different compounds exhibit strong correlations in both seasons and sizes, suggesting common sources and/or similar formation mechanisms. In $PM_{2.5}$, strong positive correlation were found between C_2 with its precursors C_3, C_4, iC_5 and ωC_2 in both seasons, with iC_4 Pyr, and MeGly in the wet season, and with Ph, ωC_3, and Gly in the dry season. Glyoxylic acid (ωC_2) correlated with Pyr in the wet season and with Gly in the dry season. These correlations suggest possible primary and/or secondary production of C_2 from aromatic and polynuclear aromatic hydrocarbons. In PM_{10}, C_2 correlated with its precursor compounds C_3, C_4, iC_5, ωC_2 and ωC_3 in both seasons, with ωC_4 and MeGly in wet season, and with Pyr and Gly in dry season. ωC_2 correlated with C_2, C_3, C_4 and iC_5 in both seasons, with Pyr in the wet season, and with Gly and MeGly in the dry season. These correlations further suggest that C_2 may be formed through chain reactions of other diacids and related compounds and/or biogenic volatile organic compounds via aqueous phase reactions.

Levoglucosan (1,6-Anhydro-β-D-glucopyranose), water-soluble K^+, organic carbon (OC) and elemental carbon (EC) are used as source tracers for biomass burning and biofuel combustion (Cachier et al., 1991, 1995; Andreae and Merlet, 2001; Puxbaum et al., 2007; Zhang et al., 2008). Table 6 shows correlation coefficients for selected diacids and related compounds against those source tracers in $PM_{2.5}$ and PM_{10} during

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the wet and dry seasons. We found strong correlations between the source tracers with diacids (C_2–C_4), iC_5 and ωC_2 (in both season), iC_4, F, Pry and MeGly (in wet season) and Ph (in dry season) in both $PM_{2.5}$ and PM_{10}. The source tracers also strongly correlated with Gly in $PM_{2.5}$ and ωC_3 in PM_{10} during both seasons, F in $PM_{2.5}$ during the wet season, M, F, mM, Gly and MeGly in PM_{10} during the dry season. These correlations suggest that the diacids, ketoacids and α-dicarbonyls are partly produced from biomass and biofuel burning in both seasons. Other studies have reported good correlation between biomass burning tracers (K^+ and EC) and diacids and related compounds (Graham et al., 2002; Kundu et al., 2010a).

Mean ratios of C_2 to C_4 and C_5 at our site can be compared with the ratios in biomass burning aerosols. The C_2/C_4 ratios in $PM_{2.5}$ were 7.0–8.3 and C_2/C_5 were 8.8–56.3 during both seasons, which are much higher than those C_2/C_4 (0.16) and C_2/C_5 (2.5) reported in aerosols associated with savannah fires in Southern Africa (Gao et al., 2003). These comparisons suggest a secondary formation of C_2 from C_4 and C_5 diacids rather than the production from biomass burning. Concentration ratios of C_2 and C_4 to non-sea-salt potassium (nss-K^+) and levoglucosan (LG) were higher (except for C_4/K^+) than those (C_2/K^+, C_2/LG; 0.05 and C_4/K^+, C_4/LG; 0.03) reported for the aerosols collected in Southern Africa savannah fires (Gao et al., 2003). These ratios suggest influence of local and regional transport of biomass burning aerosols to C_2 and C_4 diacids (Gao et al., 2003; Sillanpää et al., 2005).

We assessed the relations between total diacids with Na^+, EC, nss-K^+ and LG in $PM_{2.5}$ and PM_{10} during the wet and dry seasons. Although the air masses often originated from the Indian Ocean during the campaigns, total diacids were poorly correlated with Na^+ (tracer for sea-salt) in both seasons (Fig. 9a, b), suggesting that contributions of diacids from sea-salt aerosols are insignificant. Biomass burning has been reported to be an important source of diacids and related compounds (Kundu et al., 2010a). Strong correlations were found between total diacids with EC (Fig. 9c, d) and nns-K^+ and LG especially in the dry season (Fig. 10a–d). These relations suggest that biofuel combustion and biomass burning significantly contribute to the water-soluble organic

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species in the aerosols from Tanzania. Use of wood and charcoal for domestic cooking and heating, and field charcoal making process are common in Tanzania. In contrast, contribution of anthropogenic EC from traffic is insignificant at this rural site.

3.7 Principle component analysis for diacids, ketoacids, α-dicarbonyls and source tracers

Principal component analysis (PCA) was performed for $PM_{2.5}$ and PM_{10} data sets during the wet and dry seasons to better understand sources and/or formation processes of diacids and related compounds (Kawamura and Sakaguchi, 1999; Hsieh et al., 2008). Briefly, PCA makes use of an eigen analysis of correlation matrix of data set, after which a limited number of principal components (PCs) and their associated eigenvectors are retained and a rotation of the matrix with retained eigenvectors is carried out. The most commonly used rotation is the VARIMAX rotation of Kaiser (1958) and this rotation was used here by using statistical package SPSS version 12 (SPSS, 1988). Identification and "naming" of the VARIMAX rotated PCs in terms of aerosol source types is based on the loadings for the various variables within each PC.

Table 7 shows the VARIMAX rotated PCA resulted in two to three PCs, for the loadings for $PM_{2.5}$ and PM_{10} during the wet and dry seasons. The components explained 80.9 % and 84.4 % in $PM_{2.5}$ and 78.5 % and 88.4 % in PM_{10} of the variance in the data sets in wet and dry seasons, respectively. During the wet season for both $PM_{2.5}$ and PM_{10}, component 1 is highly loaded with C_2–C_9 diacids, ωC_2, EC, LG and OC (only in PM_{10}), whereas component 2 showed high loading of Ph, Gly and OC (only in $PM_{2.5}$). Component 1 indicates mixed sources that may be associated with photochemical oxidation of unsaturated fatty acids derived from terrestrial and/or marine plants. Higher loading of OC, EC and LG indicates an influence of biofuel combustion and biomass burning including charcoal making and burning of agricultural residues. High loading of Ph in component 2 suggests that the aromatic diacid may be derived from photooxidation of anthropogenic aromatic hydrocarbons (e.g. naphthalene) as well as oxidation of biogenic phenolic compounds (Kawamura et al., 1996a; Kawamura and Sakaguchi,

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1999). Glyoxal (Gly) may be produced by photooxidation of p-xylene (Volkamer et al., 2001), oxidation of acetylene and ethylene emitted from marine and/or anthropogenic sources (Warneck, 2003) and oxidation of isoprene from terrestrial plants (Guenther et al., 2006). Component 2 for $PM_{2.5}$ is loaded with OC suggesting mixing of air masses from natural biogenic matter and/or biomass burning aerosols.

During the dry season with $PM_{2.5}$, three PCs were obtained and associated with higher loading of C_2–C_4, ωC_2, Gly, OC and LG (component 1), C_6, Ph and EC (component 2) and C_9 (component 3). The loading of C_2–C_4 diacids indicate association with anthropogenic sources whereas ωC_2 and Gly indicate an excessive photo-oxidation of biogenic volatile organic compounds (e.g. ethane, acetylene, isoprene, and terpene) and aromatic hydrocarbons (e.g. benzene and toluene). Higher loading for OC and LG indicates that component 1 contains biomass and biofuel burning aerosols. Higher loading of C_6 diacid and Ph with component 2 suggests emissions from anthropogenic sources, whereas EC may be associated with charcoal combustion and burning of agricultural residues. Component 3 mainly loaded with C_9, which may be associated with oxidation of biogenic unsaturated fatty acids.

Similarly, three PCs were obtained in dry season for PM_{10} where component 1 was highly loaded with C_2, C_4, ωC_2, Ph, Gly, OC and LG, suggesting association with anthropogenic emissions followed by photochemical oxidation of precursor compounds. Phthalic acid and Gly may be derived from photooxidation of anthropogenic hydrocarbons (Kawamura and Sakaguchi, 1999; Ho et al., 2006) and p-xylene (Volkamer et al., 2001), respectively. These compounds may be derived from field burning of municipal solid wastes (Simoneit et al., 2005). LG is associated with biomass burning. Component 2 was loaded with C_2–C_4, C_9 and EC, suggesting photooxidation of volatile hydrocarbons, unsaturated fatty acids, and association with charcoal combustion whereas component 3 that is highly loaded with C_6 suggests photooxidation of anthropogenic emissions of hydrocarbons.

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4 Conclusions

We determined diacids, ketoacids, α-dicarbonyls and fatty acids in atmospheric aerosol samples collected between May and August 2011 from a rural site in Tanzania during the wet and dry seasons. The results on both $PM_{2.5}$ and PM_{10} showed that oxalic acid (C_2) was the dominant diacids species followed by succinic (C_4) and/or malonic (C_3) acids whereas glyoxylic acid (ωC_2) and glyoxal (Gly) were the most abundant ketoacid and α-dicarbonyls, respectively. We found higher relative abundances of oxalic acid in both seasons and sizes, adipic acid (C_6) in both sizes during the wet season, azelaic acid (C_9) in $PM_{2.5}$ during the dry season, aromatic diacids (Ph and t-Ph) in $PM_{2.5}$ during the wet season and aromatic diacids in PM_{10} during the dry season. These results suggest a possibly enhanced photochemical processing, influenced by anthropogenic and biogenic emissions as well as combustion sources. Fatty acids with even carbon number were detected with maxima of myristic acid ($C_{14:0}$) in $PM_{2.5}$ and palmitic acid ($C_{16:0}$) in PM_{10} in both seasons, indicating significant influences from biological sources. Total diacids and related compounds were present mainly in the fine fraction during both seasons (except for total α-dicarbonyls in the dry season), suggesting a larger contribution of pyrogenically and photochemically produced organic aerosols. High loadings of diacids and ratios of diacid-C/TC and diacid-C/WSOC indicate a strong influence of photochemical oxidation of organic precursors in the atmosphere during long-range transport. Strong correlations between organic components and source tracers in $PM_{2.5}$ and PM_{10} during both seasons suggest common sources and/or similar formation pathways. The correlation coefficient and principal component analysis indicated that enhanced photochemical production, biomass burning, biofuel combustion, and biogenic emissions could possibly be the sources for diacids, related compounds and their precursors.

Acknowledgements. This study was in part supported by the Environment Research and Technology Development Fund (B-0903) from the Ministry of the Environment, Japan. S. M. The authors acknowledge the financial support by the Japan Society for the Promotion of Science

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(JSPS) to S. M. We thank Mr. Filbert T. Sogomba of the Department of Physical Sciences (SUA) for sample collection. The authors also thank the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and/or READY website (http://www.arl.noaa.gov/ready.php) used in this publication.

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Table 1. Average concentrations and concentration ranges (ng m^{-3}) of diacids, ketoacids, α-dicarbonyls and fatty acids in $PM_{2.5}$ and PM_{10} during 2011 wet and dry seasons in Morogoro.

Compounds	$PM_{2.5}$								PM_{10}							
	Wet season				Dry season				Wet season				Dry season			
	Minimum	Maximum	Av.	Stdev	Minimum	Maximum	Av.	Stdev	Minimum	Maximum	Av.	Stdev	Minimum	Maximum	Av.	Stdev
Dicarboxylic acids																
Saturated straight chain diacids																
Oxalic, C_2	47.7	221.8	121.5	46.6	170.8	392.6	258.1	69.5	114.7	248.9	168.6	42.4	140.2	659.1	292.4	164.8
Malonic, C_3	5.0	23.1	11.1	5.5	16.1	36.1	25.6	7.7	14.8	49.9	26.9	10.0	20.1	95.8	42.8	28.1
Succinic, C_4	6.8	32.0	15.1	7.0	19.1	52.1	32.4	10.4	9.9	37.3	21.3	7.5	15.4	94.4	42.9	24.8
Glutaric, C_5	1.0	4.5	2.4	1.2	3.0	8.4	5.4	1.8	1.3	6.8	3.0	1.6	2.7	14.7	8.2	4.1
Adipic, C_6	2.3	6.5	4.0	1.7	9.0	35.3	18.1	7.1	1.5	4.6	2.6	1.0	2.3	25.0	6.4	5.6
Pimeric, C_7	NA*	NA*	NA*	NA*	0.9	1.3	1.1	0.2	0.9	2.8	1.5	0.9	0.1	10.4	2.7	2.2
Suberic, C_8	3.3	7.7	5.9	2.3	NA*	NA*	NA*	NA*	NA*	NA*	NA*	NA*	NA*	NA*	NA*	NA*
Azelaic, C_9	1.5	7.3	3.5	1.9	7.4	34.2	18.0	7.2	0.7	32.2	16.3	9.5	4.4	64.1	24.2	18.4
Total C_2-C_9	68.5	293.3	158.9	61.8	233.7	510.9	357.8	87.3	154.0	360.7	239.4	67.2	204.3	900.4	419.6	228.6
Unsaturated diacids																
Methylmalonic, iC_4	0.5	4.0	1.3	1.0	0.6	1.9	0.8	0.5	0.6	29.3	3.7	1.5	0.8	2.0	1.3	0.4
Methylsuccinic, iC_5	0.9	4.2	2.4	1.1	2.0	6.1	3.4	1.3	1.3	4.9	3.0	1.1	2.0	11.5	4.3	2.9
Maleic, M	0.8	1.5	1.2	0.3	2.0	4.5	3.0	0.8	0.7	2.2	1.2	0.5	1.1	6.9	2.8	2.0
Fumaric, F	1.8	5.0	3.0	1.0	1.9	5.3	3.1	1.0	1.5	4.1	2.9	1.0	2.3	7.8	4.6	1.9
Methylmaleic, mM	0.5	8.3	2.2	1.4	0.6	2.2	1.2	0.5	1.2	4.3	2.4	0.9	0.7	4.4	2.1	1.4
Phthalic, Ph	9.2	17.7	12.9	2.7	7.5	17.4	12.7	3.2	3.3	12.3	7.8	2.8	4.7	23.3	17.9	6.5
Isophthalic, iPh	0.2	3.3	1.2	1.0	0.0	0.0	0.0	0.0	0.2	7.2	3.7	2.4	0.0	0.0	0.0	0.0
Terephthalic, tPh	0.5	3.3	1.9	1.0	2.4	4.9	3.3	1.4	0.6	1.3	1.0	0.4	0.7	3.7	2.0	1.2
Total diacids	97.2	328.7	183.2	63.9	252.2	547.5	383.3	92.6	165.5	390.8	263.4	71.6	217.7	959.5	454.7	240.6
Ketocarboxylic acids																
Glyoxylic, ωC_2	5.6	23.1	12.1	5.0	17.8	40.8	29.7	8.7	8.9	23.7	13.8	4.3	11.1	58.7	29.3	13.3
3-Oxopropanoic, ωC_3	0.4	7.7	3.7	2.1	3.2	6.7	4.9	1.2	1.2	3.1	1.8	0.6	1.1	6.0	3.5	1.5
4-Oxobutanoic ωC_4	0.2	2.7	0.8	1.0	0.7	4.6	2.8	1.6	0.3	3.9	1.5	1.0	1.2	17.5	5.2	3.6
5-Oxopentanoic, ωC_5	0.4	1.5	1.0	0.5	1.3	1.9	1.6	0.3	0.4	0.4	0.4	0.0	1.0	3.7	2.1	1.4
7-Oxoheptanoic, ωC_7	0.5	7.3	3.0	2.3	2.8	8.1	5.4	2.1	1.5	8.0	3.6	2.0	2.1	10.7	5.9	2.6
8-Oxooctanoic, ωC_8	0.6	2.9	1.5	0.9	1.1	5.1	2.9	1.4	0.3	3.8	1.3	1.1	0.7	4.4	2.6	1.2
9-Oxononoic, ωC_9	0.5	13.9	6.6	4.3	5.6	11.5	7.8	2.1	2.9	47.6	18.7	12.3	6.1	41.1	22.4	14.3
Pyruvic, Pyr	1.4	6.8	2.7	1.7	1.7	7.5	4.4	1.9	1.9	8.0	3.4	1.8	1.3	16.6	7.4	5.0
Total ketocarboxylic acids	9.6	65.9	31.4	17.8	34.3	86.1	59.6	19.3	17.4	98.4	44.4	28.0	24.7	158.7	78.3	44.9
α−Dicarbonyls																
Glyoxal, Gly	2.3	13.3	5.2	3.3	2.6	7.0	4.2	1.4	4.6	9.8	6.7	1.8	3.7	13.4	7.8	3.3
Methylglyoxal, MeGly	0.01	2.8	1.4	0.9	0.2	1.0	0.5	0.3	0.3	0.9	0.6	0.2	0.1	0.8	0.4	0.3
Total α-dicarbonyls	2.9	13.3	6.4	3.0	2.6	7.3	4.4	1.7	4.9	10.6	7.3	1.9	3.7	14.1	8.0	3.5
Fatty acids																
Myristic, $C_{14:0}$	1.5	18.8	9.0	5.2	12.1	22.7	17.9	3.8	6.3	15.4	9.7	3.2	4.4	35.8	17.9	8.8
Palmitic, $C_{16:0}$	3.2	34.0	13.2	10.3	NA*	NA*	NA*	NA*	17.0	51.8	32.7	10.8	4.1	66.9	25.5	20.3
Stearic, $C_{18:0}$	1.4	7.3	4.7	1.7	1.1	8.1	3.4	2.6	6.4	23.8	13.2	6.1	2.2	11.3	4.8	3.3
Oleic, $C_{18:1}$	2.1	8.0	6.0	2.3	1.7	11.4	6.4	3.8	5.8	27.3	12.7	5.6	1.7	33.4	9.2	8.0
Arachidic, $C_{20:0}$	NA*	NA*	NA*	NA*	1.1	8.1	3.4	2.6	3.3	36.5	14.6	11.5	2.2	11.3	4.8	3.3
Behenic, $C_{22:0}$	NA*	NA*	NA*	NA*	NA*	NA*	NA*	NA*	1.1	26.4	12.0	9.9	9.9	30.0	18.1	5.6
Lignoceric, $C_{24:0}$	NA*	NA*	NA*	NA*	NA*	NA*	NA*	NA*	1.5	23.8	9.3	7.5	7.0	32.3	14.2	7.1
Total fatty acids	4.4	66.0	26.1	19.3	12.1	52.5	31.9	15.4	48.7	197.4	102.0	43.8	46.7	273.7	117.2	72.4

* Not available.

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Table 2. Relative abundances (%) of individual compound in total diacids, ketoacids, and α-dicarbonyls in $PM_{2.5}$ and PM_{10} during wet and dry seasons in Morogoro.

Compounds	$PM_{2.5}$						PM_{10}					
	Wet season			Dry season			Wet season			Dry season		
	Min	Max.	Av.	Min	Max.	Av.	Min	Max.	Av.	Min	Max.	Av.
Diacids												
Oxalic, C_2	49.0	72.1	65.4	59.4	71.7	67.1	59.3	76.0	64.6	54.1	68.7	63.9
Malonic, C_3	3.5	7.0	5.8	5.4	8.7	6.6	7.8	12.9	10.1	7.3	12.1	9.1
Succinic, C_4	6.3	9.7	8.1	6.8	9.8	8.3	6.0	9.6	8.0	7.1	10.5	9.2
Glutaric, C_5	0.9	1.8	1.3	1.1	1.9	1.4	0.6	1.7	1.1	1.1	3.5	1.9
Adipic, C_6	1.1	3.7	2.2	2.6	8.5	4.8	0.6	1.2	1.0	0.4	7.1	1.7
Pimeric, C_7	NA*	NA*	NA*	0.19	0.32	0.25	0.23	1.23	0.55	0.06	2.33	0.81
Suberic, C8	1.5	4.4	3.4	NA*	NA*	NA*	NA*	NA*	NA*	NA*	NA*	NA*
Azelaic,C_9	1.0	3.2	1.9	2.5	9.8	4.9	0.4	11.9	6.0	1.6	11.8	5.1
Methylmalonic, iC_4	0.3	1.3	0.7	0.15	0.54	0.24	0.3	11.2	1.4	0.2	0.7	0.3
Methylsuccinic, iC_5	0.8	1.9	1.3	0.6	1.3	0.9	0.8	1.8	1.2	0.7	1.2	0.9
Maleic, M	0.4	1.2	0.7	0.4	1.6	0.8	0.31	0.83	0.48	0.37	0.78	0.58
Fumaric, F	0.8	3.8	1.8	0.5	1.4	0.8	0.6	1.7	1.1	0.8	1.2	1.1
Methylmaleic, mM	0.4	5.3	1.3	0.16	0.52	0.31	0.4	1.6	0.9	0.24	0.77	0.44
Phthalic, Ph	5.0	18.2	8.0	2.4	4.0	3.3	1.9	5.1	3.0	2.2	8.0	4.5
Isophthalic, iPh	0.2	1.3	0.7	NA*	NA*	NA*	0.1	2.4	1.4	NA*	NA*	NA*
Terephthalic, tPh	0.2	2.6	1.4	0.52	0.90	0.71	0.27	0.33	0.29	0.20	0.67	0.44
Ketoacids												
Glyoxylic, ωC_2	30.9	83.2	46.9	38.2	56.4	50.7	14.4	47.2	34.4	29.0	67.9	43.4
3-Oxopropanoic, ωC_3	4.0	18.9	12.0	5.4	10.5	8.5	2.0	6.5	4.7	3.5	7.0	5.0
4-Oxobutanoic ωC_4	0.9	4.7	2.2	1.9	8.9	4.7	0.5	7.5	3.8	1.4	21.5	6.1
5-Oxopentanoic, ωC_5	1.0	4.4	2.4	1.8	3.8	2.5	NA*	NA*	NA*	1.2	2.9	2.0
7-Oxoheptanoic, ωC_7	2.5	14.6	9.2	7.2	12.4	9.0	2.5	14.1	8.8	6.1	12.8	8.5
8-Oxooctanoic, ωC_8	3.0	6.2	4.8	2.8	7.3	4.7	0.4	6.7	3.0	2.2	6.0	3.8
9-Oxononoic, ωC_9	1.7	40.2	23.9	7.7	18.0	13.8	8.6	76.8	37.3	9.1	48.5	28.0
Pyruvic	5.3	18.2	9.4	4.2	14.7	7.6	3.1	23.9	8.8	4.7	30.8	11.4
α-Dicarbonyls												
Glyoxal, Gly	61.0	100.0	79.5	85.2	100.0	95.0	88.0	94.1	92.0	93.1	100.0	98.2
Methylglyoxal, MeGly	0.2	39.0	25.0	3.0	14.8	10.0	5.9	12.0	8.0	1.1	6.9	3.7

* Not available.

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Table 3. Comparison between average concentrations of diacids, ketoacids, and α-dicarbonyls in atmospheric aerosols from Morogoro, Tanzania and different sites around the world.

Compounds Compounds	[a]Morogoro, Tanzania $PM_{2.5}$, wet and dry	[a]Morogoro, Tanzania PM_{10}, wet and dry	[b]Nylsvley, South Africa TSP, dry	[c]Sapporo, Japan TSP, spring and summer	[d]Tokyo, Japan TSP, one year	[e]Salzburg, Austria TSP, summer	[f]Chennai, India PM_{10}, winter and summer	[g]Nainital, India TSP, winter and summer	[h]Hong Kong, China TSP, spring and summer	[i]Jeju Island, Korea TSP, one year
Diacids										
Oxalic, C_2	189.8	230.5	79.2	192	270	15.3	360	284	373	473
Malonic, C_3	18.4	34.9	51.7	77	55	22	52	23.2	68.4	67
Succinic, C_4	23.8	32.1	13.1	58	37	14	39	26	52.5	52
Glutaric, C_5	3.9	5.5	1.9	13	11	2.7	10	5.7	13.5	11
Adipic, C_6	11.1	4.5	2.6	5.1	16	4.4	7.2	6.6	11.7	8.4
Pimeric, C_7	0.8	2.1	1.3	2.6	5.3	–	5.2	2.2	2.3	2.6
Suberic, C_8	3.0	–	1.8	1.1	8.4	–	8.2	0.6	2.3	2.6
Azelaic,C_9	10.8	20.3	5.0	6.5	23	–	21	9.8	12.9	4.7
Methylmalonic, iC_4	1.1	2.5	–	1.6	2.5	–	1.4	1.1	3.2	1.1
Methylsuccinic, iC_5	2.9	3.7	–	3.9	5.1	–	3.8	2.6	7.2	–
Maleic, M	2.1	2.0	–	4.1	5.6	–	2.1	2.3	16.2	4.9
Fumaric, F	3.1	3.8	–	2.1	3.7	–	1.3	2.3	3.3	5.2
Methylmaleic, mM	1.7	2.3	–	2.8	3.8	–	2.1	1.9	6.5	5.3
Phthalic, Ph	12.8	12.9	1.5	17		3.3	21	4.7	83.9	9.8
Isophthalic, iPh	1.2	3.7	–	0.7		–	1.7	2.5	14.1	
Terephthalic, tPh	2.6	1.5	–	2.6		–	52	4.3	–	–
Subtotal	289	362	158.1	390	446	61.7	588	359	671	648
Ketoacids										
Glyoxylic, ωC_2	20.9	21.6	–	22	39	–	32	15.8	30.9	36
3-Oxopropanoic, ωC_3	4.3	2.7	–	0.46	3.0	–	3.8	3.3	0.66	1.7
4-Oxobutanoic ωC_4	1.8	3.4	–	0.97	3.6	–	5.7	4.0	3.0	2.5
9-Oxononoic, ωC_9	7.2	20.6	–	2.1	2.3	–	2.1	10.5	2.6	1.4
Pyruvic, Pyr	3.6	5.4	5.6	9.6	6.7	2.6	6.8	5.9	2.4	13
Subtotal	37.8	53.7	5.6	35.1	54.6	2.6	50.4	39.5	39.6	54.6
***α*-Dicarbonyls**										
Glyoxal, Gly	4.7	7.3	10.8	4.6	12	9.6	4.6	6.1	2.7	0.5
Methylglyoxal, MeGly	1.0	0.5	–	5.1	21	–	5.5	2.5	8.2	11
Subtotal	5.7	7.8	10.8	9.7	33	9.6	10.1	8.6	10.9	11.5

[a]This study.
[b]Limbeck et al. (2001).
[c]Aggarwal and Kawamura (2008).
[d]Kawamura and Ikushima (1993).
[e]Limbeck et al. (1999).
[f]Pavuluri et al. (2010).
[g]Hegde and Kawamura (2012).
[h]Ho et al. (2006).
[i]Kawamura et al. (2004).

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Table 4. Correlation coefficients (r^2) for selected diacids and related compounds in $PM_{2.5}$ during wet season (upper diagonal triangle) and dry season (lower diagonal triangle) at Morogoro. Positive correlation coefficients ≥ 0.55 are indicated in bold.

	C_2	C_3	C_4	iC_4	iC_5	M	F	mM	Ph	Pyr	ωC_2	ωC_3	ωC_4	ωC_9	Gly	MeGly
C_2		**0.96**	**0.94**	**0.64**	**0.72**	0.53	0.26	0.02	−0.02	**0.81**	**0.88**	0.46		0.09	0.53	**0.66**
C_3	**0.74**		**0.98**	**0.69**	**0.78**	0.50	0.25	−0.42	0.13	**0.81**	**0.94**	0.51		0.21	**0.61**	0.53
C_4	**0.88**	**0.76**		**0.75**	**0.79**	0.43	0.41	−0.29	0.20	**0.89**	**0.93**	0.51		0.17	**0.67**	**0.72**
iC_4	0.22	0.04	0.42		0.34	0.39	**0.83**	−0.29	0.56	**0.81**	**0.71**	0.26		0.07	**0.89**	0.01
iC_5	**0.63**	**0.58**	**0.86**	0.33		0.25	0.05	−0.43	−0.18	**0.56**	**0.69**	0.13		0.03	0.25	**0.55**
M	−0.20	−0.34	−0.10	0.35	−0.01		0.05	−0.04	−0.13	0.33	0.30	0.36		0.44	0.11	−0.28
F	0.45	0.09	0.38	0.10	0.41	0.19		0.26	0.49	**0.67**	0.31	0.19		−0.08	**0.71**	0.01
mM	0.34	0.27	0.32	0.41	0.42	0.13	0.38		−0.17	−0.10	−0.36	**0.61**		−0.14	−0.22	0.32
Ph	**0.63**	**0.77**	**0.75**	0.25	0.52	−0.11	−0.22	−0.05		0.37	0.32	**0.61**		0.27	**0.69**	0.10
Pyr	0.38	0.20	0.49	**0.60**	0.31	−0.05	−0.04	0.26	0.31		**0.79**	**0.59**		0.00	**0.72**	**0.70**
ωC_2	**0.90**	**0.67**	**0.66**	−0.06	0.31	−0.28	0.36	0.15	0.55	0.24		0.54		0.28	**0.76**	**0.68**
ωC_3	**0.74**	0.46	0.52	0.22	0.07	−0.34	−0.02	−0.02	**0.58**	0.47	**0.82**			**0.61**	0.39	0.45
ωC_4	0.27	0.37	0.48	0.31	0.28	**0.72**	−0.16	−0.20	**0.79**	**0.56**	0.24	0.34		NA*	NA*	NA*
ωC_9	0.25	**0.75**	0.25	−0.30	0.03	−0.36	−0.25	−0.24	**0.58**	−0.07	0.39	0.26	0.41		0.24	0.12
Gly	**0.84**	0.38	**0.76**	0.30	0.53	−0.01	0.50	0.28	0.46	0.54	**0.79**	**0.70**	0.38	−0.10		0.52
MeGly	0.40	0.25	0.36	0.43	0.03	**0.73**	−0.64	−0.43	**0.86**	0.39	−0.14	0.09	0.50	0.49	0.52	

* Not available.

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Table 5. Correlation coefficients (r^2) for selected diacids and related compounds in PM_{10} during wet season (upper diagonal triangle) and dry season (lower diagonal triangle) at Morogoro. Positive correlation coefficients ≥ 0.55 are indicated in bold.

	C_2	C_3	C_4	iC_4	iC_5	M	F	mM	Ph	Pyr	ωC_2	ωC_3	ωC_4	ωC_9	Gly	MeGly
C_2		**0.90**	**0.92**	−0.05	**0.65**	0.24	0.30	0.29	0.44	0.42	**0.93**	**0.96**	**0.70**	−0.13	0.04	**0.55**
C_3	**0.94**		**0.85**	0.06	0.51	0.17	0.18	0.43	0.39	0.42	**0.78**	**0.80**	0.53	0.10	−0.08	0.26
C_4	**0.95**	**0.95**		−0.15	**0.78**	0.32	0.39	0.35	0.53	**0.57**	**0.92**	**0.92**	**0.70**	−0.03	0.08	0.54
iC_4	0.53	0.52	0.52		−0.26	−0.29	−0.44	−0.16	−0.30	−0.28	0.00	−0.19	−0.17	−0.14	−0.40	−0.48
iC_5	**0.92**	**0.91**	**0.96**	**0.55**		**0.75**	**0.66**	**0.60**	**0.66**	**0.86**	**0.79**	**0.79**	0.47	−0.37	0.53	**0.62**
M	**0.95**	**0.99**	**0.97**	0.46	**0.94**		**0.88**	**0.76**	**0.85**	**0.77**	0.31	0.38	0.04	−0.48	**0.89**	**0.60**
F	**0.92**	**0.93**	**0.98**	0.43	**0.91**	**0.95**		**0.60**	**0.90**	**0.58**	0.31	0.49	0.15	−0.33	**0.84**	**0.74**
mM	**0.82**	**0.92**	**0.91**	0.43	**0.89**	**0.94**	**0.92**		**0.57**	**0.73**	0.29	0.08	−0.17	−0.01	**0.64**	0.21
Ph	0.50	0.38	0.52	−0.32	0.40	0.39	0.51	0.34		**0.62**	0.41	0.53	0.27	−0.36	**0.72**	**0.74**
Pyr	**0.62**	**0.71**	**0.63**	0.42	0.44	0.53	**0.74**	**0.72**	0.50		**0.57**	0.49	0.34	−0.39	0.51	0.37
ωC_2	**0.95**	**0.90**	**0.96**	0.24	**0.92**	**0.91**	**0.91**	**0.79**	**0.67**	0.43		**0.94**	**0.76**	−0.25	0.10	**0.55**
ωC_3	**0.93**	**0.85**	**0.92**	0.22	**0.81**	**0.85**	**0.91**	**0.70**	**0.69**	0.45	**0.95**		**0.80**	−0.45	0.22	**0.75**
ωC_4	0.15	0.02	0.20	−0.06	0.17	−0.02	0.15	−0.10	0.54	−0.14	0.32	0.33		−0.32	−0.12	0.47
ωC_9	−0.29	−0.36	−0.36	−0.63	−0.23	−0.33	−0.52	−0.45	0.13	−0.70	−0.15	−0.31	−0.18		−0.31	−0.35
Gly	**0.93**	**0.91**	**0.94**	0.21	**0.83**	**0.91**	**0.92**	**0.80**	**0.68**	**0.58**	**0.95**	**0.96**	0.20	−0.26		**0.67**
MeGly	0.52	0.46	**0.66**	0.19	**0.66**	0.48	**0.59**	0.40	**0.81**	−0.40	**0.63**	**0.56**	**0.78**	**0.55**	**0.59**	

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Table 6. Correlation coefficients (r^2) for selected diacids and related compounds against source tracers (organic carbon, OC; elemental carbon, EC; non-sea-salt potassium, nss-K^+, and levoglucosan, LG) in $PM_{2.5}$ and PM_{10} during wet and dry seasons at Morogoro. Correlation ≥ 0.55 are bolded.

Species	$PM_{2.5}$								PM_{10}							
	Wet season				Dry season				Wet season				Dry season			
	OC	EC	Nss-K^+	LG	OC	EC	Nss-K^+	LG	OC	EC	Nss-K^+	LG	OC	EC	Nss-K^+	LG
C_2	0.46	**0.76**	−0.20	**0.66**	**0.75**	0.27	**0.74**	**0.66**	**0.68**	**0.76**	**0.65**	**0.57**	**0.75**	**0.90**	**0.65**	**0.78**
C_3	**0.55**	**0.77**	−0.09	**0.69**	**0.79**	0.28	0.51	0.43	**0.61**	**0.60**	0.47	0.54	**0.61**	**0.90**	0.53	**0.69**
C_4	**0.63**	**0.83**	−0.10	**0.72**	**0.87**	0.54	**0.77**	**0.74**	**0.85**	**0.86**	**0.74**	**0.68**	**0.69**	**0.95**	0.51	**0.74**
iC_4	**0.58**	**0.69**	−0.25	0.33	0.13	0.16	0.17	0.18	−0.27	−0.32	−0.01	−0.12	0.04	0.31	−0.17	0.20
iC_5	0.48	**0.76**	−0.11	**0.96**	**0.87**	**0.55**	**0.65**	**0.85**	**0.79**	**0.79**	**0.56**	**0.70**	**0.69**	**0.93**	0.43	**0.80**
M	−0.18	0.40	−0.66	0.29	−0.06	0.20	0.12	0.16	0.32	0.28	−0.09	0.22	**0.64**	**0.91**	0.51	**0.72**
F	0.35	**0.62**	−0.09	0.07	0.27	0.34	0.54	0.48	0.34	0.24	−0.10	0.10	**0.63**	**0.92**	0.45	**0.65**
mM	−0.11	−0.19	−0.02	−0.29	0.40	−0.23	0.28	0.54	0.20	0.18	−0.18	0.16	**0.59**	**0.88**	0.41	**0.68**
Ph	0.49	0.09	0.23	−0.20	**0.70**	0.49	0.50	0.37	0.43	0.35	0.03	0.20	**0.55**	0.43	**0.55**	0.43
ωC_2	**0.69**	**0.68**	−0.01	**0.58**	**0.58**	0.21	**0.70**	0.45	**0.77**	**0.87**	**0.78**	**0.66**	**0.72**	**0.87**	**0.60**	**0.76**
ωC_3	0.32	0.25	0.22	0.08	0.30	0.02	0.43	0.16	**0.80**	**0.85**	**0.77**	**0.64**	**0.65**	**0.82**	0.59	**0.61**
ωC_4	NA*	NA*	NA*	NA*	0.50	**0.57**	**0.57**	0.34	**0.64**	**0.75**	**0.72**	0.48	0.21	0.23	0.04	0.18
ωC_9	0.17	−0.03	−0.17	0.03	0.33	0.20	0.12	−0.15	−0.09	−0.12	−0.16	−0.18	0.05	−0.31	0.19	0.06
Pyr	**0.64**	**0.87**	0.02	0.51	0.38	0.08	0.46	0.36	**0.58**	**0.59**	0.34	0.53	0.30	0.43	0.32	0.26
Gly	**0.68**	**0.56**	0.05	0.18	**0.64**	0.42	**0.88**	**0.73**	0.04	0.13	−0.30	−0.10	**0.69**	**0.84**	**0.66**	**0.67**
MeGly	**0.72**	0.33	0.11	**0.58**	−0.27	0.22	−0.28	−0.42	0.42	**0.58**	0.29	0.18	**0.71**	**0.63**	0.33	**0.63**

* Not available.

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Table 7. Varimax with Kaiser normalization rotated principal component matrix for selected diacids, ketoacids, α-dicarbonyls, and source tracers in $PM_{2.5}$ and PM_{10} during 2011 wet and dry season at Morogoro. High (> 0.60) and very high (> 0.90) loadings are indicated in bold.

Compounds	Wet season				Dry season					
	$PM_{2.5}$		PM_{10}		$PM_{2.5}$			PM_{10}		
	Comp 1	Comp 2	Comp 1	Comp 2	Comp 1	Comp 2	Comp 3	Comp 1	Comp 2	Comp 3
C_2	**0.9**	0.16	**0.91**	0.15	**0.95**	0.16	−0.17	**0.69**	**0.68**	−0.19
C_3	**0.91**	0.29	**0.87**	0.05	**0.6**	0.58	−0.05	0.54	**0.79**	−0.02
C_4	**0.91**	0.36	**0.97**	0.2	**0.83**	0.48	0.06	**0.63**	**0.77**	−0.02
C_6	**0.63**	0.42	**0.77**	0.16	−0.03	**0.98**	0.09	−0.04	0.04	**0.95**
C_9	**0.82**	0.22	**0.73**	0.13	−0.06	−0.02	**0.97**	−0.03	**0.88**	0.07
Ph	−0.14	**0.95**	0.36	**0.87**	0.51	**0.71**	0.1	**0.82**	0	0.33
ωC_2	**0.81**	0.51	**0.91**	0.15	**0.83**	0.08	−0.45	**0.78**	0.58	−0.05
Gly	0.38	**0.84**	−0.08	**0.95**	**0.9**	0.03	−0.18	**0.73**	**0.61**	0.05
OC	0.46	**0.66**	**0.89**	0.09	**0.75**	0.58	0.13	**0.85**	0.24	−0.2
EC	**0.84**	0.17	**0.87**	0.13	0.19	**0.74**	−0.25	0.39	**0.87**	−0.02
LG	**0.9**	−0.12	**0.8**	−0.13	**0.78**	0.23	0.2	**0.8**	0.33	−0.19
Variance	7.1	1.8	7	1.6	6.3	1.8	1.2	7.4	1.2	1.1
Variance%	64.8	16.1	63.7	14.8	57.2	16.5	10.7	67.1	11.3	10

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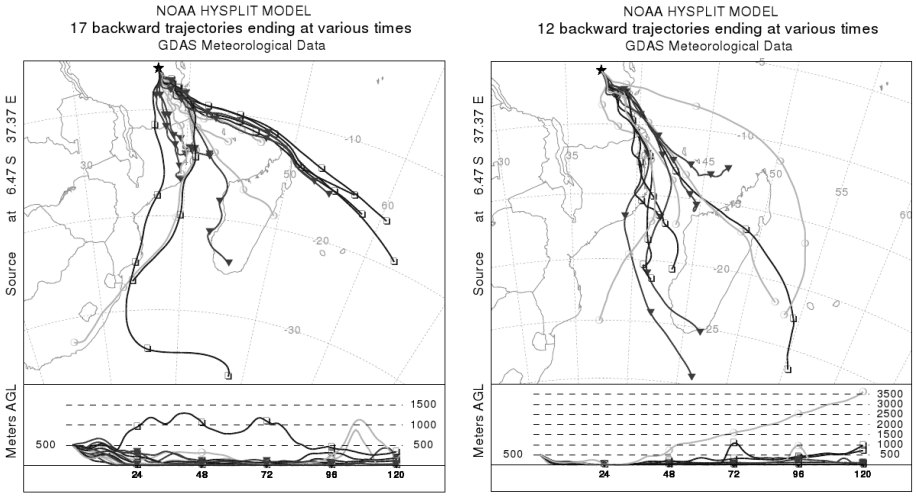

Wet season Dry season

Fig. 1. Five-day backward air mass back trajectories arriving at Morogoro during the wet and dry seasons.

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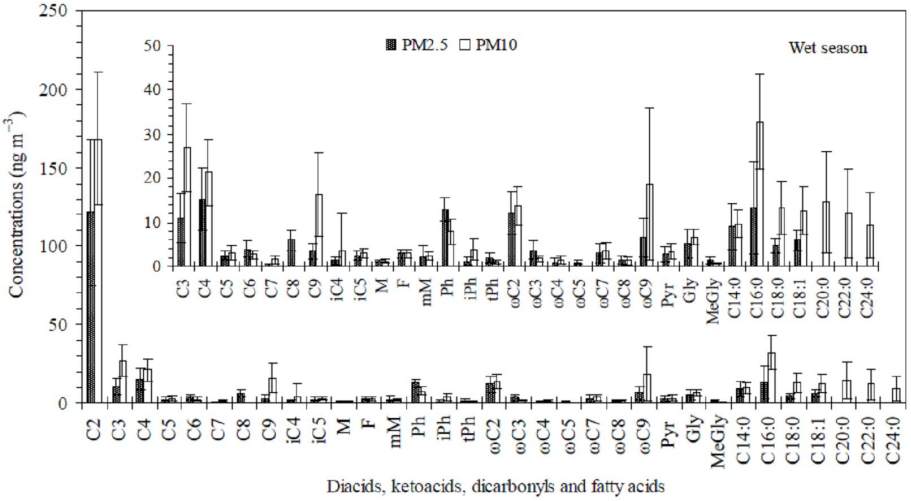

Fig. 2. Size distributions and average molecular compositions of diacids, ketoacids, α-dicarbonyls and fatty acids in aerosols from Morogoro during 2011 wet season. See Table 1 for abbreviations.

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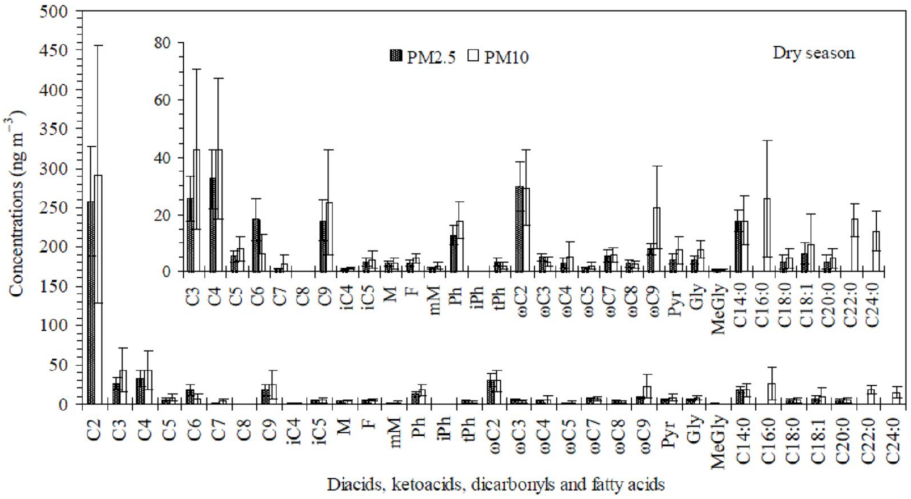

Fig. 3. Size distributions and average molecular compositions of diacids, ketoacids, α-dicarbonyls and fatty acids in aerosols from Morogoro during 2011 dry season. See Table 1 for abbreviations.

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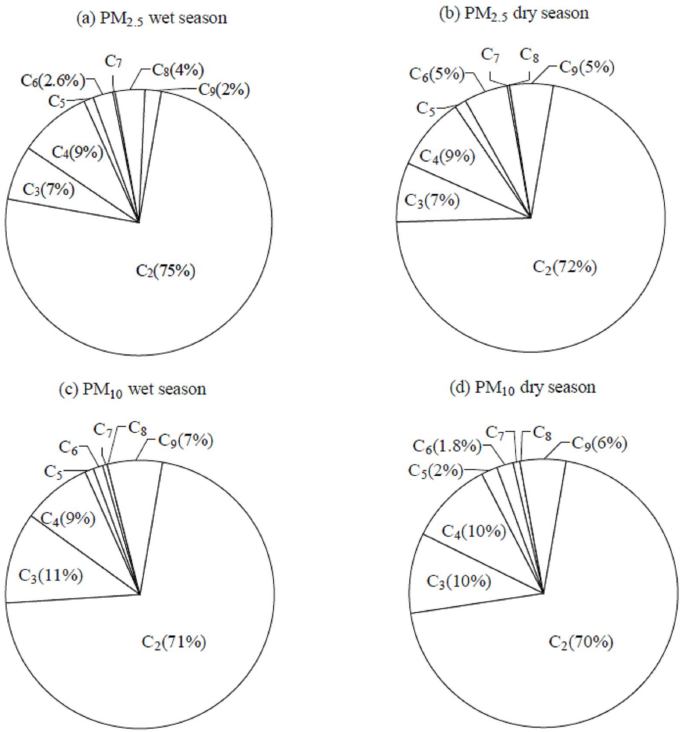

Fig. 4. Size distributions of relative abundances (%) of individual diacids in total straight-chain diacids (C_2–C_9) in aerosols collected in wet **(a, c)** and dry **(b, d)** seasons in Morogoro.

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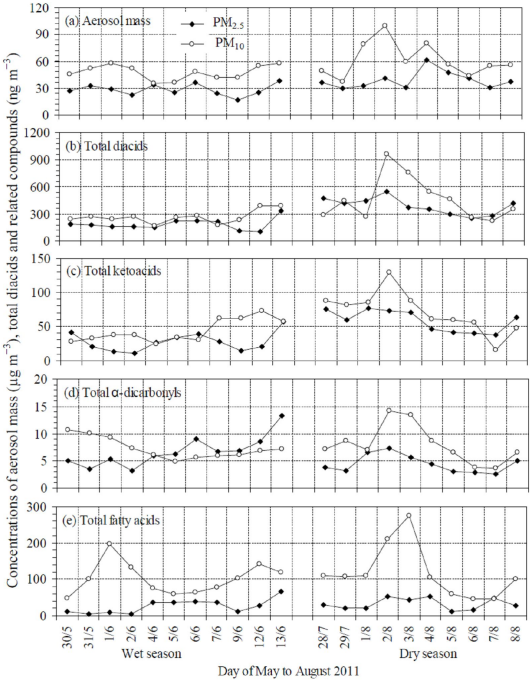

Fig. 5. Temporal variations of the concentrations of **(a)** aerosol mass, **(b)** total diacids, **(c)** total ketoacids, **(d)** total α-dicarbonyls, and **(e)** total fatty acids in $PM_{2.5}$ and PM_{10} during 2011 wet and dry seasons.

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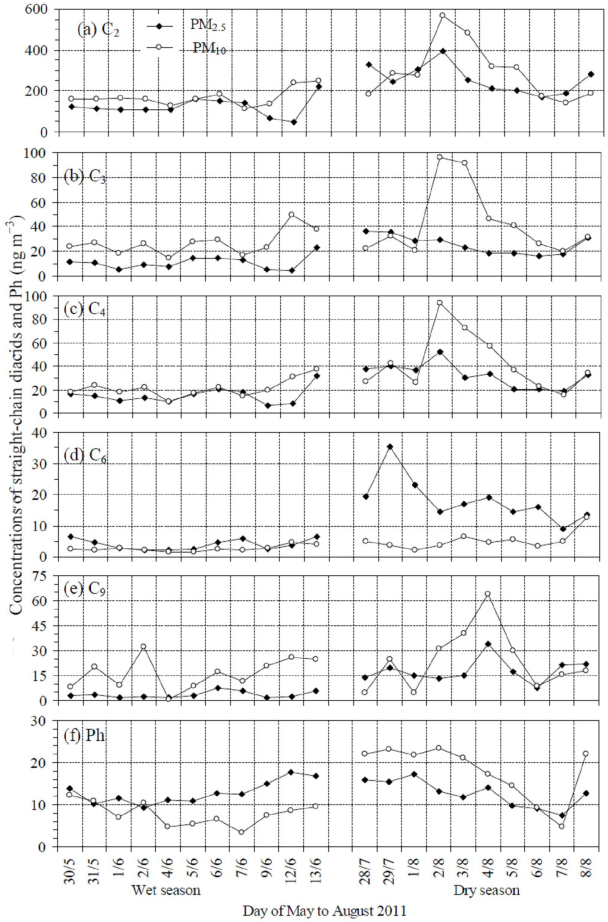

Fig. 6. Temporal variations of the concentrations of **(a)** oxalic acid (C_2), **(b)** malonic acid (C_3), **(c)** succinic acid (C_4), **(d)** adipic acid (C_6), **(e)** azelaic acid (C_9) and **(f)** phthalic acid (Ph) in $PM_{2.5}$ and PM_{10} during 2011 wet and dry seasons.

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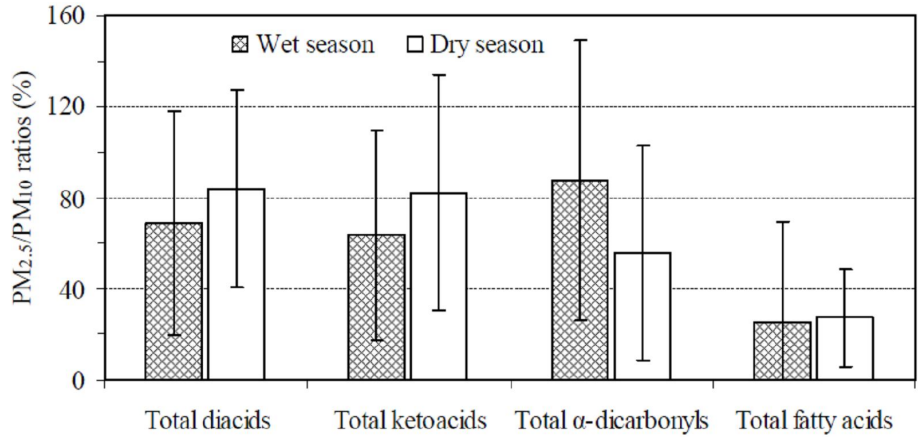

Fig. 7. Mean concentration ratios (%) of total diacids, ketoacids and α-dicarbonyls in $PM_{2.5}$ to those in PM_{10} during the 2011 wet and dry season campaigns in Morogoro.

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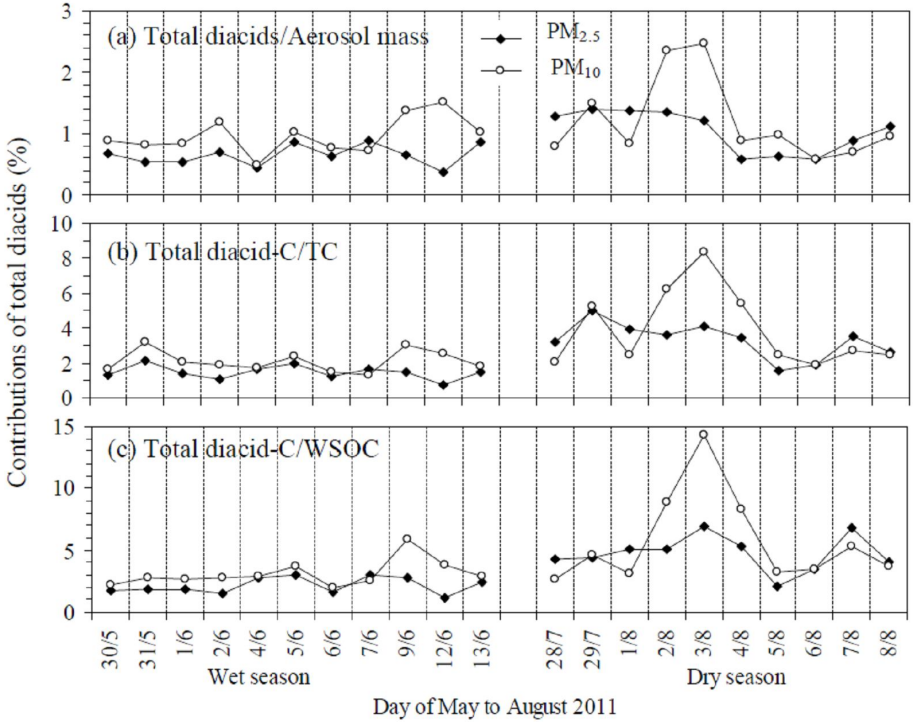

Fig. 8. Temporal variations in contributions (%) of total diacids to **(a)** aerosol mass, **(b)** total carbon (TC), and **(c)** water-soluble organic carbon (WSOC) in $PM_{2.5}$ and PM_{10} during 2011 wet and dry seasons.

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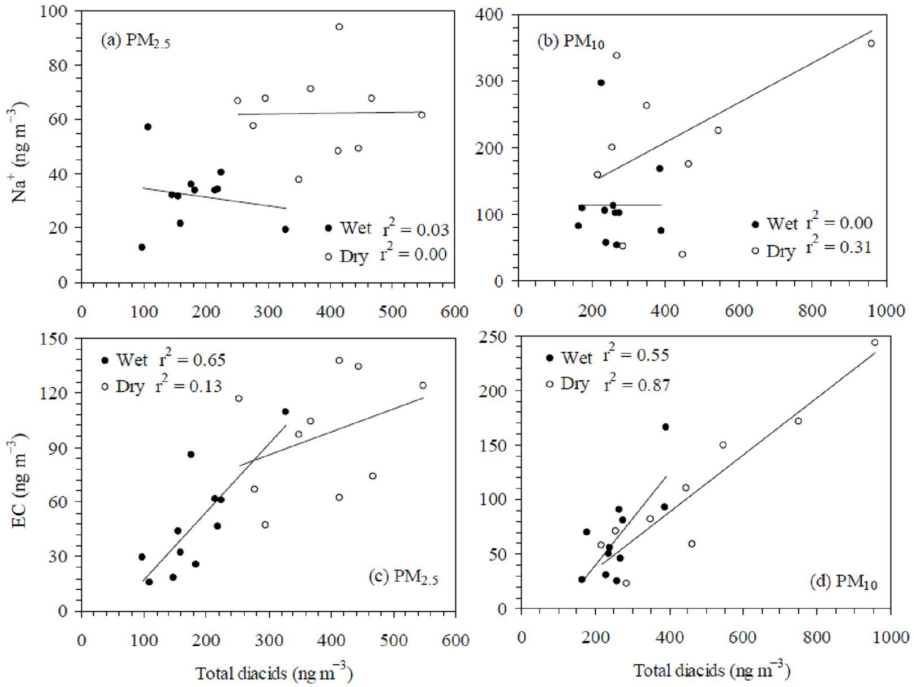

Fig. 9. Correlation between total diacids with Na^+ and EC in $PM_{2.5}$ **(a, c)** and PM_{10} **(b, d)** at Morogoro during the wet and dry seasons.

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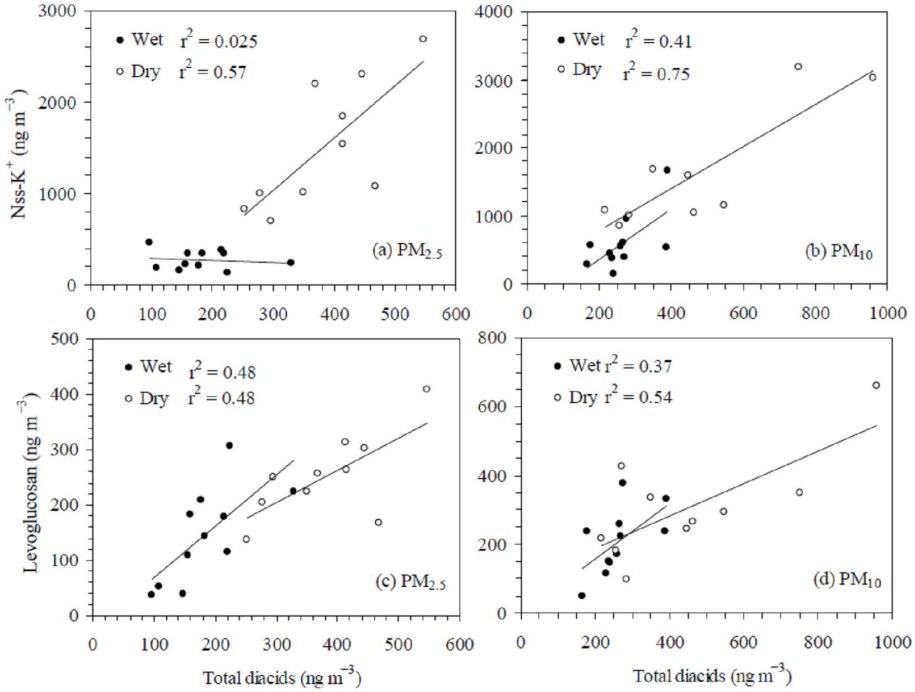

Fig. 10. Relations between total diacids with nss-K^+ and levoglucosan in $PM_{2.5}$ **(a, c)** and PM_{10} **(b, d)** during the wet and dry seasons in Morogoro.

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