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Characteristics of Low-Molecular Weight Carboxylic Acids in PM_{2.5} and PM₁₀ Ambient Aerosols From Tanzania

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Additional information is available at the end of the chapter

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1. Introduction

Carboxylic acids together with water-soluble inorganic ions are an important group of water-soluble organic compounds in the atmospheric aerosols (Jacobson et al., 2000; Bourotte et al., 2007). They are highlighted because they account for substantial portion of atmospheric aerosols, and potentially control chemical and physical properties of the particles. Consequently, they may have direct and indirect effects on the earth's radiation balance by scattering incoming solar radiation, which counteracts the global warming (IPCC, 2007). More attention has been paid to carboxylic acids due to their potential to modify the hygroscopic properties of atmospheric particles, including cloud condensation nuclei activity and hence to change global radiation balance (Kerminen, 2001; Peng et al., 2001). Major water-soluble inorganic ions are associated with atmospheric visibility degradation, adverse human health effects, and acidity of precipitation (Dockery & Pope, 1996; IPCC, 2007).

Among the organic acids, low molecular weight carboxylic acids such as acetic, oxalic and malonic are generally most abundant in the atmospheric aerosols. Carboxylic acids in variable concentrations have been reported in various environments including rural and urban atmosphere (Kawamura & Sakaguchi, 1999; Kerminen et al., 2000; Nicolas et al., 2009) and have different source origin, including biomass burning, fossil fuel combustion (Kawamura 1987; Narukawa et al., 1999), sea spray, traffic and industrial emissions and photochemical oxidation of precursors from anthropogenic and biogenic origin (Kawamura & Sakaguchi, 1999; Limbeck & Puxbaum, 1999; Kumar et al., 2001; Chakraborty & Gupta, 2010). Other sources for carboxylic acids in the marine atmosphere include in-cloud and heterogeneous formations (Warneck, 2003).

Chemical composition of PM_{2.5} and even that of PM₁₀ aerosols is important to gain insights into sources and of their toxicity and to evaluate effectiveness of abatement strategies for relevant emission sectors. Particulate matter (PM) with aerodynamic diameter less than 2.5 μm (PM_{2.5}) exhibited stronger relation with health than those with aerodynamic diameter less than 10 μm (PM₁₀), but other studies have reported a strong potential of PM₁₀ to human health (Salma et al., 2002; Kappos et al., 2004). Most studies on low molecular weight carboxylic acids and their related compounds (Limbeck et al., 2001; Limon-Sanchez et al., 2002; Kawamura & Yasui, 2005) and major ions (Harrison et al., 2004; Karthikeyan & Balasubramanian, 2006; Mariani et al., 2007; Kundu et al., 2010; Mkoma et al., 2010) have extensively been reported.

In Africa similar aerosols measurements especially of organic components are missing. Therefore, a full scenario of air quality is far from being revealed because some pollutants including carboxylic acids have not been measured. The knowledge of elucidating chemical composition, levels, and source profiles of aerosols in the Tanzania atmosphere remains a challenge and is needed for both scientific and policy reasons. The continuous changes in socioeconomic and political environments in Tanzania result in changes in development, particularly in transport, industry, energy, and construction sectors. This chapter reports for the first time in Tanzania, composition of low molecular weight carboxylic acids in PM_{2.5} and PM₁₀ aerosol samples collected from a rural background atmosphere in Morogoro. An insight of characteristics of water-soluble inorganic ions is also discussed in this chapter.

2. Experimental

2.1. Aerosol sampling site

Aerosol samples were collected at a rural site in Morogoro (300,000 inhabitants) between 26 April and 10 May 2011. This site is located at about 200 km west of the Indian Ocean and the city of Dar es Salaam, a business capital in Tanzania (Fig. 1). The samples were collected at Solomon Mahlangu Campus of Sokoine University of Agriculture (06°47'41"S, 37°37'44"E, altitude 504 m a.s.l.). This site is located about 5 km from Morogoro central area and major road systems and possible aerosol sources include biomass burning, agriculture, livestock and soil dust. Approximately 70% of this area is covered by vegetation and about 15% with pasture field. Conversely, tropical savannah is the most important land cover in large part of the sampling site.

2.2. Aerosol collection

Two samplers were used in parallel to collect aerosol particles: a "Gent" PM_{2.5} and PM₁₀ filter holder each with two quartz fibre filters (Whatman QM-A) in series. Quartz fibre filters can adsorb volatile organic compounds (VOCs) causing positive artifacts when measuring PM and particulate OC. On the other hand, semi-volatile organic compounds (SVOCs) in aerosols may partially evaporate during sampling resulting in negative artifacts (Turpin et al., 2000; Mader et al., 2003; Hitzenberger et al., 2004). The quartz fibre filters were pre-fired

at 550 °C during 24 h before use. Samplers operated at a flow rate of 17 L/min and were mounted on grass survey at SMC synoptic station approximately 2.7 m above ground level. The sampling was carried out approximately in 24 h intervals and exchange of filters during sampling periods was done at 7:30 am. A total of 11 sets of actual filed samples and 2 blanks were collected for each sampler and used in this chapter. After sampling the exposed filters were folded in half face to face, placed in polyethylene plastic bags and kept frozen at -4 °C during storage and transported cool to the laboratory of research and development in chemistry (LPQ) at the Institute of chemistry, Federal University of Bahia (UFBA). The samples were stored in a freezer at -20 °C prior to analysis. All the procedures were strictly quality-controlled to avoid any possible contamination of the samples.

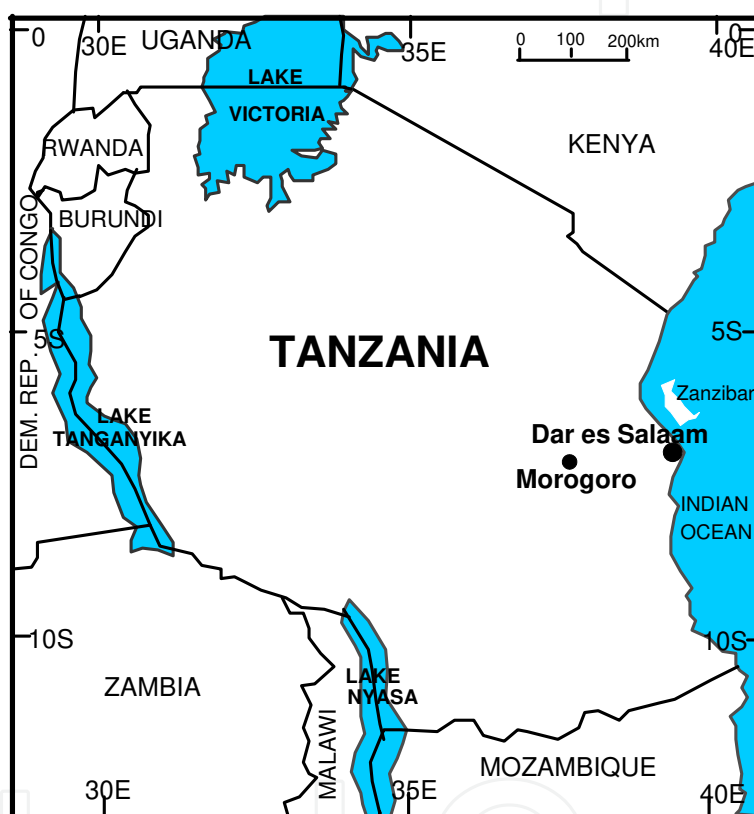


Figure 1. Location of the sampling site in Morogoro, Tanzania

During the sampling period meteorological data were collected from the site. The daily winds were predominantly south-easterly with an average speed of 6.8 m/s. Average temperature was 26.8 °C and average relative humidity was 73%. The recorded maximum temperature and relative humidity were 29.8 °C and 79.5%, while minimum values were 23.7 °C and 63.5%, respectively. During the campaigns 5 days hand rainfall of a total 19.9 mm.

2.3. Aerosol analyses

For particulate mass measurements, the filter samples were weighed before and after sampling with an analytical microbalance balance Mettler Toledo MX5 (reading precision 1 µg). Before weighing, the filters were conditioned in a chamber equipped with hydro-

thermometer clock at a temperature of 20 °C and relative humidity of 40% for 48 h and the weightings were done under these conditions.

For determination of carboxylic acids and water-soluble ions one-half of 12.88 cm² portions punched from of each PTFE filter was extracted using 5 ml Milli-Q ultrapure water (resistivity of 18.2 MΩcm, Barnstead International, USA) in a shaker tubes Model AT56 (Fanem Ltd, Sao Paulo, Brazil) for 5 minutes, followed by filtering through Polytetrafluoroethylene (PTFE) filter (0.45 µm pore size, Sartorius Stedim, Germany). The concentrations of aqueous extracts were determined by Dionex ion chromatography ICS 1100 and ICS 2100 for acids/anions and cations respectively which was equipped with an auto sampler (Dionex ICS Series AS-DV). An analytical column AS16 (3 × 50 mm) with AG16 guard column (3 × 50 mm) and CSRS-300 I (2 mm) suppressor in ion-exchange mode was used to determine carboxylates (monocarboxylates: formate and acetate; dicarboxylates: oxalate, malonate, succinate, and maleate; ketocarboxylate: pyruvate) and water-soluble anions (chloride Cl⁻, nitrate NO₃⁻ and sulphate SO₄²⁻). The eluent gradient programme was sweeping from 6.0 to 8.0 mmol/L KOH in 35 minutes under flow rate of 0.38 µL/min, except for acetic acid which was determined in another run, reducing injection time to avoid overlap of peaks. For determination of water-soluble cations (NH₄⁺, Na⁺, K⁺, Mg²⁺ and Ca²⁺) an analytical column CS16 and Guard column CG16 (both 3 × 50 mm) and CSRS-I (2 mm) suppressor in a chemical mode were used. An eluent of 17.5 mmol/L H₂SO₄ was used at flow rate of 0.35 µL/min. The injection volume was 25 µL for all detection. Peak identification was confirmed based on a match of ion chromatograph retention times and standard samples. Limit of detection determined as mean equal to 3 times standard deviation of the field blank value corresponded to a range of 0.008 to 0.017 ng/L for carboxylates, 0.008 to 0.023 ng/L for anions and 0.021 to 0.083 ng/L for cations. Limits of quantification were between 0.026 and 0.058 ng/L for carboxylates, 0.028 and 0.078 ng/L for anions and 0.063 and 0.252 ng/L for cations.

3. Results and discussion

3.1. Concentrations of PM mass

Mean PM mass concentrations and associated standard deviations and ranges as derived from the two low-volume samplers are shown in Table 1. The results showed that mean mass concentration of PM_{2.5} and PM₁₀ aerosols during the campaign were 13±3.5 µg/m³ and 16±2.3 µg/m³, respectively. The percentages of PM_{2.5} mass in PM₁₀ size fraction (Fig. 2) found to range from 44–99% with a mean of 83±29%. These results indicate that most of PM mass was in PM_{2.5} size fraction. High PM_{2.5}/PM₁₀ ratios for PM mass indicate that there is small contribution from soil dust, which is known to be mostly associated with PM₁₀ aerosols. Currently in Tanzania, the ambient air quality standard limit values for inhalable particulate matter are 60 to 90 µg/m³ for PM₁₀ (TBS, 2006). The mean concentrations for PM₁₀ mass at our site in Morogoro were below these average limit values. In addition, the current data sets were in line with levels reported in our previous studies (Mkoma et al., 2009a,b; Mkoma et al., 2010). Nevertheless, when compared PM mass data from our rural

site in Tanzania are in line with few available other data sets for rural sites in Southern Africa (Nyanganyura et al., 2007). They are also comparable to or lower to other sites in Europe and Asia (Van Dingenen et al., 2004; Gu et al., 2010; Maenhaut et al., 2011; Ram & Sarin, 2011).

3.2. Concentrations of carboxylates ions

Table 1 present mean total concentrations and range of carboxylates (TCAs) which were 23.7 ± 6.5 ng/m³ (range: 13.3-36.5 ng/m³) in PM_{2.5} and 36.4 ± 12 ng/m³ (range: 10.7-58.2 ng/m³) in PM₁₀ aerosols. Oxalate and malonate were most abundant carboxylates in PM_{2.5} accounting for 32.5% and 31.85% of total carboxylates, respectively, whereas in PM₁₀ acetate was most abundant accounted for 62.5% of total carboxylates followed by oxalate which accounted for 32.6% of total carboxylates. Other studies have also reported oxalates to be most abundant carboxylate in aerosol samples (Mochida et al., 2003; Warneck, 2003). Pyruvate was also found in substantial amount and formate the least abundant counting on average 3% of total carboxylates in each of the aerosol fractions. Succinate and malonate were below detection limit in PM_{2.5} and PM₁₀ aerosols, respectively. The total carboxylates accounted for 0.18% to total PM_{2.5} mass and 0.22% to PM₁₀ mass. In comparison with other studies, the mean concentrations of all measured carboxylates in Tanzania were lower to those reported in urban and rural sites around the world (Souza et al., 1999; Kerminen et al., 2000; Yao et al., 2003; Kawamura & Yasui, 2005).

3.3. Water-soluble inorganic ions and ratios

Chemical characteristics of water-soluble inorganic ions and their relative abundances in PM_{2.5} and PM₁₀ aerosols are also shown in Table 1. In both aerosol fractions, water-soluble Mg²⁺ was the most important cation and SO₄²⁻ the main anionic species. On average Mg²⁺ accounted for 44.4% of total water-soluble ions in PM_{2.5} and 24.7% in PM₁₀ whereas SO₄²⁻ accounted for 22.8% and 35.2% of total ions in PM_{2.5} and PM₁₀, respectively. High levels of crustal element Mg²⁺ together with Ca²⁺ are essentially attributable to soil/mineral dust dispersal. As to reasonable NH₄⁺ levels (8% of total ions) in PM_{2.5}, this may be due to presence of ammonia gas from biomass burning especially during smoldering combustion (Andreae & Merlet, 2001) and from agricultural activities in particular cattle raising (Street et al., 2003; Stone et al., 2010). Water-soluble K⁺, a good indicator for biomass burning, was second most abundant cation in PM_{2.5} accounted for 10.6% of total water-soluble ions.

For SO₄²⁻ the higher levels could be attributed to its efficient formation by in-cloud processing of SO₂ (Yao et al., 2003) and from secondary formation processes (Allen et al., 2004). As to low NO₃⁻ levels, this is likely due to the fact that the site is rural with little or no traffic and undoubtedly there are less anthropogenic emissions of precursor gas NO_x. Also as to low concentrations of Na⁺ which is mainly derived from sea-salt, this is presumably due to long distance (about 200 km) from the Indian Ocean to our sampling site. The observed levels for water-soluble ions are comparable with those reported in our previous work in Morogoro (Mkoma et al., 2009a; Mkoma et al., 2010). It appears that the levels of

SO_4^{2-} , NO_3^- , and NH_4^+ in PM10 fractions are substantially lower in Tanzania than at European rural sites (Putaud et al., 2004) and Asia (Aggarwal & Kawamura, 2009; Pavuluri et al., 2011).

Species	PM2.5					PM10				
	Mean	SD	Min.	Max.	Rel. Ab.	Mean	SD	Min.	Max.	Rel. Ab.
PM mass ($\mu\text{g}/\text{m}^3$)	13.3	3.5	8.2	19.5	-	16.2	2.3	12.5	20.5	-
Carboxylates ions (ng/m^3)										
Formate, FA	0.71	0.30	0.38	1.27	3.00	1.2	0.6	0.5	2.6	3.4
Acetate, Ac	5.4	2.2	0.4	7.8	22.9	22.7	3.3	16.3	27.5	62.5
Oxalate, Oxa	7.7	2.7	4.7	13.1	32.5	11.8	7.2	4.5	31.0	32.6
Malonate, Mal	7.5	3.9	4.8	18.3	31.8	-	-	-	-	-
Succinate, Suc	-	-	-	-	-	1.6	2.4	0.2	6.5	4.5
Pyruvate, Pyr	2.4	0.7	1.5	3.8	9.9	2.2	0.7	0.9	3.3	6.1
Total carboxylate	23.7	6.5	13.3	36.5	-	36.4	12.0	10.7	58.2	-
Water-soluble ions (ng/m^3)										
NH_4^+	37.8	11.7	21.0	66.5	8.4	26.2	12.5	10.7	54.0	4.1
NO_3^-	4.5	1.6	1.2	8.0	1.0	25.1	12.4	10.5	52.0	3.9
SO_4^{2-}	102	27	69.1	160	22.8	237	125	38.8	487	36.6
Cl^-	2.3	0.4	1.6	3.1	0.5	9.6	5.7	3.3	20.2	1.5
Na^+	15.6	2.5	13.2	21.5	3.5	98.5	42.0	41.1	174.8	15.2
K^+	47.5	24.1	22.0	97.0	10.6	37.6	28.2	6.3	88.5	5.8
Mg^{2+}	199	33.7	155	265	44.4	158	69	16.4	228	24.5
Ca^{2+}	39.3	8.5	28.1	58.8	8.8	56.2	42.9	1.0	107	8.7
Total ions	448	88	348	585	-	646	214	256	1108	-

Rel. Ab. = Relative abundances

Table 1. Mean concentrations, ranges and relative abundances (%) of carboxylates and water-soluble inorganic ions in PM2.5 and PM10 aerosols from Morogoro.

To determine the impact of marine sources on chemical composition of aerosol particles in PM2.5 and PM10 fractions, sea-salt ratios were calculated for each inorganic ion using Na as a reference element, assuming all Na to be of marine origin. The ratios for Cl^-/Na^+ , $\text{SO}_4^{2-}/\text{Na}^+$, K^+/Na^+ , $\text{Mg}^{2+}/\text{Na}^+$ and $\text{Ca}^{2+}/\text{Na}^+$ in PM2.5 were 0.15 (0.25), 6.48 (1.81), 2.95 (0.04), 12.97 (0.04), 2.44 (0.12), respectively. The corresponding values in PM10 were 0.10 (0.25), 2.51 (1.81), 0.43 (0.04), 1.68 (0.04), 0.75 (0.12), respectively. Values in brackets represent average ratios for each ion in sea-water (Brewer, 1975). Larger ratios of ions indicate incorporation of non-marine constituents in aerosols. As to low mean Cl^-/Na^+ ratios than sea-water ratio indicates that a minor fraction of Na^+ may be contributed from other sources such as mineral dust. But also low ratio could be due to modifications of sea-salt fraction by non-marine constituents. Chloride loss may be explained by

heterogeneous reaction of airborne sea-salt with acidic gases and aerosol species (Millero, 2006).

3.4. Time series of PM mass and selected aerosol species

Time series of PM mass, selected acids and ions species in PM_{2.5} and PM₁₀ fractions as a function of sampling time are shown in Figs. 2 and 3. Nss-SO₄²⁻ in Fig. 2 was hereby obtained by subtracting sea-salt contribution from measured SO₄²⁻ data. Sea-salt contribution of SO₄²⁻ was obtained as 0.252Na⁺, whereby Na⁺ is the measured concentration of Na⁺ and 0.252 is SO₄²⁻/Na⁺ ratio in the bulk seawater composition given by Riley and Chester (1971). As can be observed in Fig. 2, selected species in both size fractions showed no clear trends that can be noted but showed slightly variation during sampling period especially for PM₁₀ aerosols. The observed behaviour of the species could be resulted from variations in sources strengths and meteorological conditions, such as mixing height. Additionally, high relative humidity (mean: 73%) during the campaign could serve as removal mechanisms hence lead to a daily variation in carboxylates levels.

In this study, oxalate concentrations were high to a factor of 10 than those of formate during the sampling period and in both PM_{2.5} and PM₁₀ aerosol particles. These results indicate that formate was mainly from photochemical oxidation, while oxalates might have other sources besides photochemical oxidation. On the other hand, the concentrations of acetate were high than those of oxalate. Acetic acid in the atmosphere has been reported to be produced by oxidations of longer-chain dicarboxylic acids (Kawamura et al., 1996). Therefore, the observed acetate levels suggest that longer-chain dicarboxylic acids were possibly available at our site. Unfortunately, no data for high molecular weight dicarboxylic acids measured for the campaign.

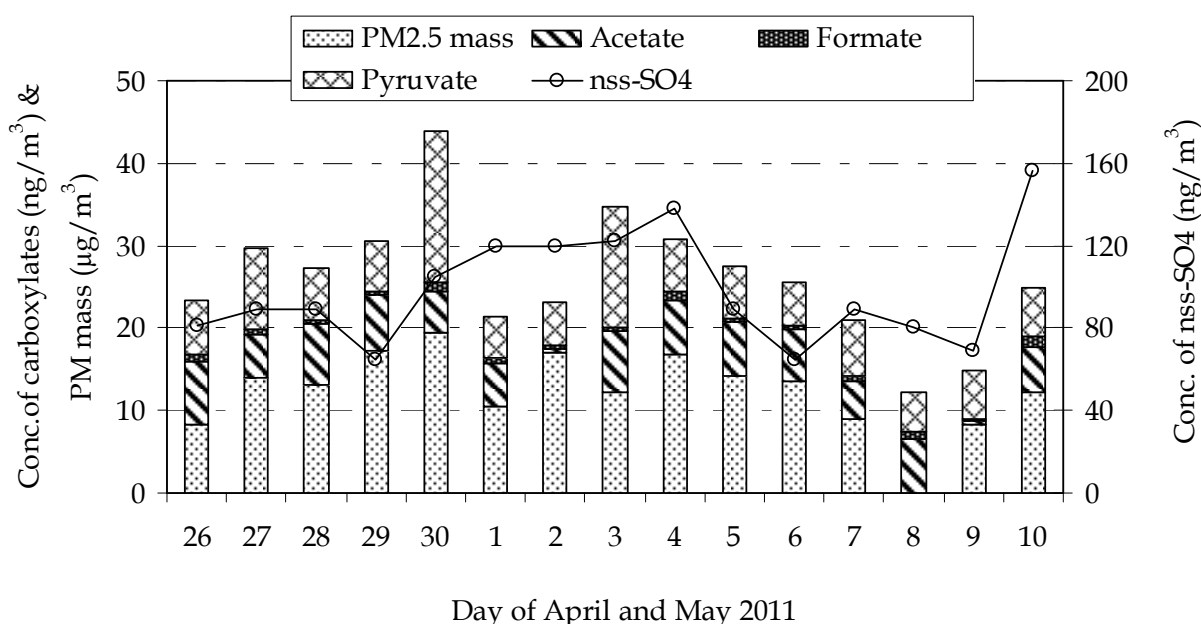


Figure 2. Time series of PM mass, carboxylates and nss-SO₄²⁻ in PM_{2.5} fraction at Morogoro

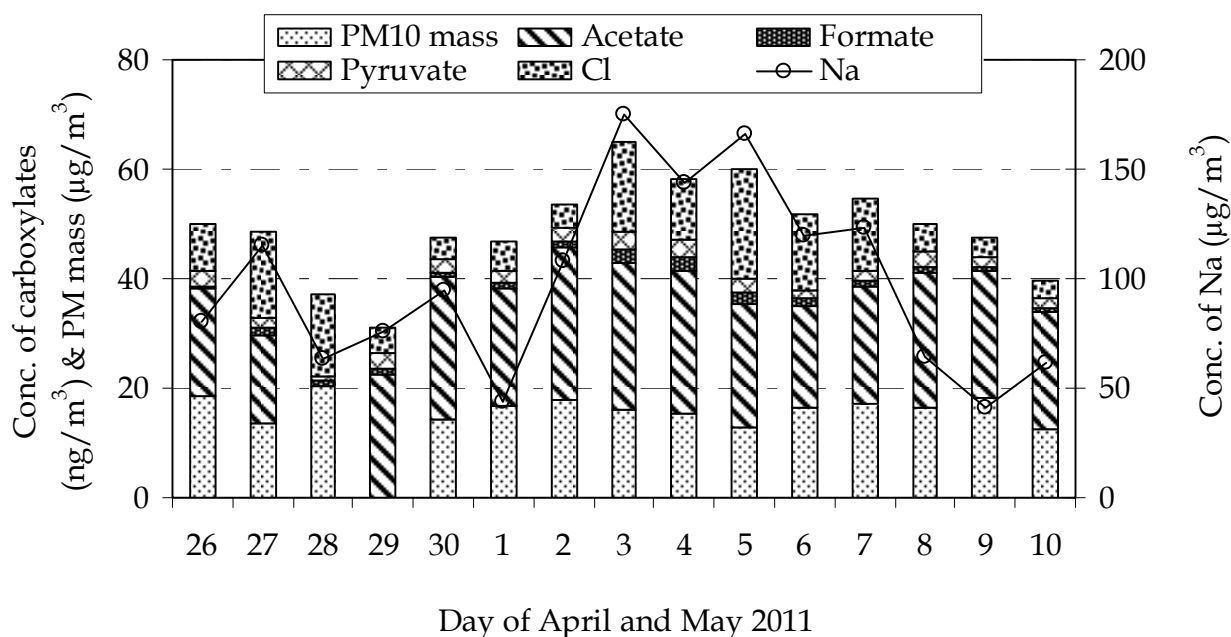


Figure 3. Time series of PM mass, carboxylates and Na^+ and Cl^- in PM10 fraction at Morogoro

3.5. PM2.5 to PM10 ratios

The average PM2.5 (fine) to PM10 (coarse) percentage ratios and associated standard deviations for PM mass, carboxylates and various water-soluble inorganic ions are shown in Fig. 4. The ratios were calculated on the basis of data for PM2.5 and PM10 samples taken in parallel and then averaged over all samples from the sampling period. The mean fine to coarse ratios for all species with exception of those for acetate, Na^+ , Ca^{2+} , NO_3^- and Cl^- were predominantly associated with fine fraction (for more than 55%). High fine/coarse ratio for PM mass may be due to a less contribution from soil dust, which is known to be mostly associated with coarse particles. For carboxylates, high ratios (even larger than 70%) are considered to be attributed from secondary organic aerosols (SOA), biomass burning activities and high temperature (average: 26.8 °C during sampling period). Concentrations of oxalate in PM2.5 showed strong correlations ($r^2 = 0.70$) with those in PM10 aerosols. The slope of linear regression equations ($\text{PM2.5} = 2.48 \times \text{PM10}$) indicated that oxalate was mainly present in fine fraction during sampling period. On the other hand, different size distributions between oxalate and acetate could be related to their different physical characteristics. Acetate in PM2.5 fraction could easily volatilize (more volatile than oxalate) to gas phase, part of which could be absorbed on PM10 particles.

For water-soluble inorganic ions, as expected, sea-salt elements (Na , Cl) and indicator element for crustal matter (Ca) were predominantly (for more than 62%) associated with PM10 aerosols. NH_4^+ and nss-SO_4^{2-} were mainly present in the fine aerosols suggesting that these species originated from high temperature sources and/or gas-to-particle conversion. The nss-SO_4^{2-} is due to oxidation of SO_2 , which is predominantly from anthropogenic origin (e.g. biomass burning). A well-known indicator for biomass burning, K was associated with the fine particles (about 100%) suggesting vegetative

emissions and crustal source could be an important source for K⁺ aerosols at this site with small impact from biomass burning activities.

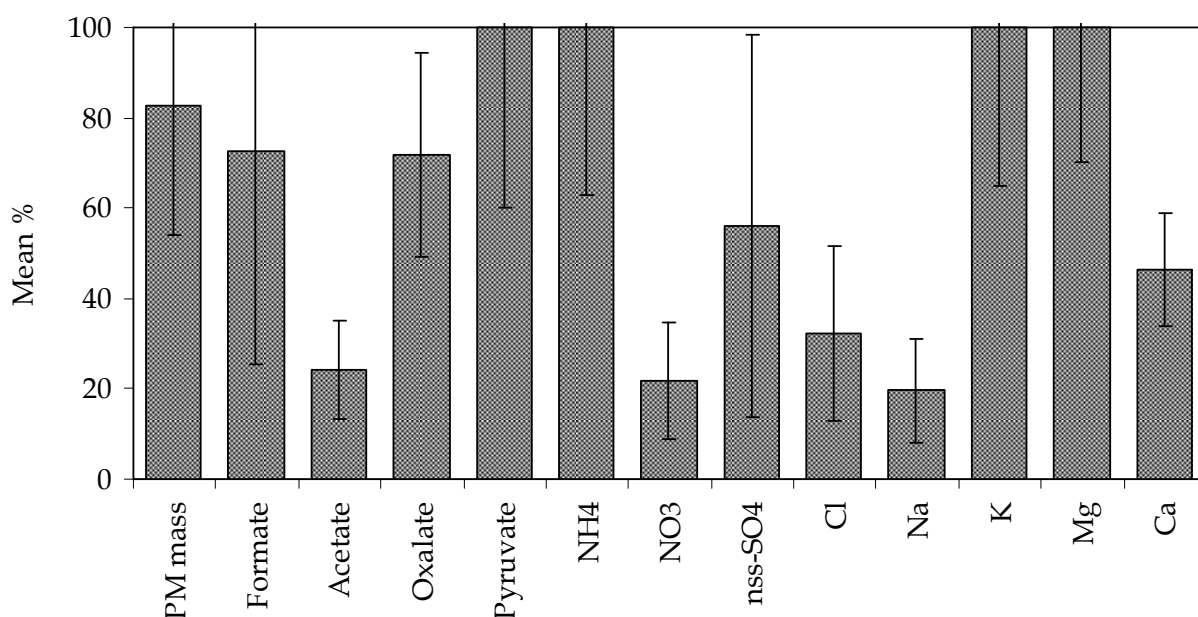


Figure 4. Mean contribution (%) of PM_{2.5} aerosols mass and selected aerosol species in PM₁₀ fraction during the campaign in Morogoro.

3.6. Sources of carboxylates and water-soluble ions in aerosols

3.6.1. Correlation analysis

Correlation coefficients of PM mass, carboxylates and source indicators, shown in Table 2 were performed in order to understand their possible sources and formation mechanisms. The selected source indicators include K⁺ for biomass burning and vegetation emissions, Na⁺ and Cl⁻ for sea spray or waste burning, and SO₄²⁻ for secondary formation of different mechanisms. Temperature and wind speed have been used as additional parameters to illustrate the atmospheric behaviours of carboxylic acids. In this study K⁺ had good correlation with formate ($r^2=53$) and moderate to poorly correlations with other carboxylates in PM₁₀. This indicates that formate could be originated from biomass and/or waste burning emissions but other carboxylates are considered to have other important sources than biomass burning. It can also be observed from Table 2 that there were possible similar sources for formate and other carboxylates (oxalate, Succinate and pyruvate) as verified by good correlation between them in PM_{2.5} and PM₁₀ aerosols. Pyruvate shows good correlation with acetate ($r^2 = 54$) and succinate ($r^2=51$) in PM₁₀ aerosols. These indicate a feature of photochemical decomposition of succinic acid (Yao et al., 2002).

Sea-salt derived aerosols have been reported to have particle with aerodynamic diameter between 1 and 5 μm (Kerminen et al., 2000). In this study, we found Na⁺ has pronounced

amount in PM₁₀ aerosol and to slightly extent Cl^- , suggesting sea spray could be one of the contributing sources of the aerosol components at the site. But even though Na^+ correlate well ($r^2=73$) with Cl^- , the calculated Cl^- to Na^+ mass ratio to sea-salt component in aerosol particles had mean value between 0.15 (PM_{2.5}) and 0.10 (PM₁₀). This suggest that continental contributions was most important than marine contribution since Cl^-/Na^+ ratio in marine aerosols varies between 1.0 and 1.7 (Chesselet et al., 1972).

Sulphate has been used as reference to investigate major formation routes of carboxylic acids (Yu et al., 2005). As shown in Table 2, formate and pyruvate showed good correlation with SO_4^{2-} in PM_{2.5}, suggesting that in-cloud and heterogeneous formations play an important role in the formation of carboxylates. On the other hand, poor correlation of malonic with SO_4^{2-} in PM_{2.5} suggests that possibly the acid is volatile at ambient temperatures (Peng et al., 2001). Acetate and oxalate showed poor correlations with SO_4^{2-} in both aerosol fractions, indicating that they mainly originated from primary emissions sources and/or the atmospheric processes different from those of SO_4^{2-} . This is contrary to what have been observed in other studies that in-cloud and heterogeneous formations can yield a good correlation between oxalate and SO_4^{2-} (Yu et al., 2005).

Wind speed poorly correlated with most carboxylates except with acetate ($r^2=51$) in PM₁₀ aerosols. This indicates that in addition to secondary formation carboxylates were mainly generated from local sources, while acetate might be related to long range aerosols transport to the sampling site. It should also be noted that primary emissions are major sources of precursors for most carboxylic acids (Kawamura & Yasui, 2005).

Species	FA	Ac	Oxa	Mal	Suc	Pyr	SO_4^{2-}	NO_3^-	Cl^-	Na^+	K^+	Ca^{2+}	WS
FA		0.26	0.10	0.19	–	0.91	0.60	0.31	0.10	–	0.38	–	-0.23
Ac	0.42		0.21	0.11	–	0.28	-0.04	0.45	0.27	–	-0.09	–	-0.21
Oxa	0.77	0.29		0.31	–	0.11	0.34	0.23	0.17	–	0.30	–	-0.07
Mal	–	–	–		–	0.17	0.17	0.51	0.33	–	0.13	–	0.08
Suc	0.57	0.42	-0.11	–		–	–	–	–	–	–	–	–
Pyr	0.48	0.54	0.13	–	0.51		0.52	0.21	-0.01	–	0.31	–	-0.20
SO_4^{2-}	–	0.26	0.30	–	0.31	-0.10		-0.16	-0.06	–	0.93	–	0.06
NO_3^-	0.88	0.17	0.74	–	0.55	0.30	0.11		0.78	–	-0.41	–	-0.03
Cl^-	0.55	-0.29	0.56	–	0.28	-0.11	0.05	0.81		–	-0.26	–	-0.12
Na^+	0.81	0.18	0.74	–	0.39	0.36	0.23	0.87	0.73		–	–	–
K^+	0.53	0.35	0.38	–	0.45	0.45	0.22	0.39	0.18	0.45		–	-0.02
Ca^{2+}	0.65	0.23	0.52	–	0.30	0.32	0.25	0.58	0.32	0.58	0.51		–
WS	-0.10	0.51	0.25	–	-0.44	-0.23	0.28	-0.06	-0.08	-0.19	0.11	0.26	

WS = Wind speed

Table 2. Correlation coefficients for PM mass, carboxylates, selected ions and wind speed in PM_{2.5} (upper diagonal triangle) and PM₁₀ fractions (lower diagonal triangle) in Morogoro. Correlation coefficients that are larger than 0.50 are indicated in bold.

3.6.2. Concentrations ratios

The ratio of acetic to formic acid has been used as good indicator of contributions of primary (high ratio) and secondary sources (low ratio) to carboxylic acids (Talbot et al., 1988, 1990; Grosjean, 1992). As can be seen in Table 3, low acetate/formate ratios for both PM2.5 and PM10 aerosols particles indicate that secondary formation was an important contributing source of carboxylates at our site. This suggestion is supported by the fact that high mean average temperature during sampling period (mean: 26.8 °C) might be controlling factor in determining the contribution of primary and secondary sources to these carboxylates. However, there are various types of the atmospheric reactions forming carboxylic acids (e.g. formic, acetic, and oxalic) in urban and near urban atmospheres, which include oxidation of unsaturated fatty acids originating from cooking activities, ozone oxidation of olefins emitted from vehicular exhausts (Scheff & Wadden, 1993) and oxidation of aromatic hydrocarbons (Kawamura & Ikushima, 1993).

The ratio of oxalic acid to total dicarboxylic acid (for this study oxalic, malonic, succinic acids) can be used to evaluate aging process of organic aerosols (Kawamura & Sakaguchi, 1999), because diacid such as oxalic acid can be produced by oxidations of longer-chain dicarboxylic acids (Kawamura et al., 1996). In this study oxalate to total dicarboxylates ratios show low values in both aerosol fractions, indicating that aerosols emitted from various sources and transported to this site were less and equally aged. Since there relative humidity was high during the campaign (up to 73% on average), it is supposed that oxalate was also produced in aqueous phase. Aqueous phase chemistry in aerosol and/or cloud droplets is important in production of oxalic acid (Warneck, 2003). On the other hand, mean ratio of oxalate to K⁺ in PM2.5 aerosols was 0.19±0.08, somewhat close to or higher than those reported range (0.03–0.1) for flaming and smoldering phases in burning plumes (Yamasoe et al., 2000). This suggests that carboxylates might be originated from biogenic sources with contribution from biomass burning emissions.

Ratio	PM2.5		PM10	
	Mean±Stdev	Range	Mean±Stdev	Range
Acetate/Formate	0.24±0.31	0.07–1.07	0.05±0.03	0.03–0.10
Oxalate/Total dicarboxylates	0.33±0.08	0.23–0.49	0.33±0.17	0.15–0.83
Oxalate/K ⁺	0.19±0.08	0.07–0.36	–	–

Table 3. Mean ratios and ranges for carboxylates and K⁺ in PM2.5 and PM10 aerosols in Morogoro.

4. Conclusion

PM2.5 and PM10 aerosols samples were collected from a rural site Morogoro, Tanzania and analysed for low molecular weight carboxylates and water-soluble inorganic ions. Oxalate and malonate were dominant species in PM2.5 while acetate was most prominent species in

PM10 aerosols followed by oxalate. Of the ionic components, SO_4^{2-} , K^+ , and Mg^{2+} in PM2.5 and SO_4^{2-} , Na^+ , and Mg^{2+} in PM10 made larger contribution to total water-soluble inorganic aerosol mass. Various ratios and correlations between carboxylates and ions used for possible source identification suggest that primary emissions, secondary formation, and to a slightly extent sea spray and biomass burning could be the sources for the aerosols at this site. The ratio of acetate to formate was used to distinguish primary and secondary sources of these carboxylates and was found to be close to reported value for secondary reactions, indicating dominance of secondary sources. Substantial concentration of carboxylates and water-soluble ions observed in the Morogoro atmosphere suggest that it was urgent to study the characteristics and sources of these species to better understand their roles in the Tanzania environment. However, more work is needed to determine longer-chain (high) molecular weight carboxylic acids and related organic compounds and their seasonal variations in other urban and rural sites in Tanzania.

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