

Stable carbon and nitrogen isotopic compositions of tropical atmospheric aerosols: sources and contribution from burning of C₃ and C₄ plants to organic aerosols

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(Manuscript received 27 November 2012; in final form 29 November 2013)

ABSTRACT

In this paper, we report for the first time the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ data for $\text{PM}_{2.5}$ and PM_{10} aerosols collected in Tanzania during May–August 2011 together with total carbon (TC) and nitrogen (TN) contents. Mean TC concentrations were $6.5 \pm 2.1 \mu\text{g m}^{-3}$ in $\text{PM}_{2.5}$ and $9.2 \pm 3.5 \mu\text{g m}^{-3}$ in PM_{10} . $\delta^{13}\text{C}$ of TC ranged from -26.1 to -20.6‰ with a mean of -23.6‰ in $\text{PM}_{2.5}$ and from -24.4 to -22.4‰ with a mean of -23.6‰ in PM_{10} . We found substantially greater $\delta^{13}\text{C}$ values in $\text{PM}_{2.5}$ samples during dry season as well as strong positive correlation between levoglucosan (and nss-K⁺) and TC in $\text{PM}_{2.5}$. These results suggest a significant contribution from burning of C₄ plants to fine organic aerosol formation. TN contents showed a mean of $0.7 \pm 0.3 \mu\text{g m}^{-3}$ in $\text{PM}_{2.5}$ and $0.8 \pm 0.2 \mu\text{g m}^{-3}$ in PM_{10} . $\delta^{15}\text{N}$ ranged from $+13.4$ to $+22.1\text{‰}$ with a mean of $+16.2 \pm 2.7\text{‰}$ in $\text{PM}_{2.5}$ and $+10.4$ to $+18.7\text{‰}$ with a mean of $+13.7 \pm 2.2\text{‰}$ in PM_{10} . $\delta^{15}\text{N}$ showed higher ratios in fine particles than coarse particles in both wet and dry season. The relatively high $\delta^{15}\text{N}$ values suggest isotopic enrichment of ^{15}N in aerosols via exchange reaction between NH_3 (gas) and NH_4^+ (particle). We found a strong correlation between TN and NH_4^+ ($r^2 = 0.94$ in $\text{PM}_{2.5}$ and $r^2 = 0.86$ in PM_{10}) and NO_3^- ($r^2 = 0.48$ in $\text{PM}_{2.5}$ and $r^2 = 0.55$ in PM_{10}). We also found that organic nitrogen is less significant than inorganic nitrogen in the Morogoro aerosols. Based on stable carbon isotopic composition, contributions of burning C₃ plants to TC were estimated to range from 42 to 74% in $\text{PM}_{2.5}$ and from 39 to 64% in PM_{10} , whereas those of C₄ ranged from 26 to 58% in $\text{PM}_{2.5}$ and from 36 to 61% in PM_{10} . These results suggest that burning activities of C₃ and C₄ plants contribute to organic aerosol formation in Tanzania.

Keywords: $\text{PM}_{2.5}$ and PM_{10} , aerosols, isotopic composition of total carbon and nitrogen, C₃ and C₄ plants, Tanzania

1. Introduction

Stable carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotopic compositions can provide complementary information about sources of aerosols and have long been applied in various environments (Turekian et al., 1998; Lajtha and Marshall, 1999; Narukawa et al., 2008; Pavuluri et al., 2010). Also, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of bulk aerosols have been used to better understand the contributions of various sources to organic aerosols including biomass and biofuel burning (Ballentine

et al., 1998; Martinelli et al., 2002; Widory, 2007). In tropical sites, biomass burning is widespread as it serves to convert forests to agricultural and pastoral lands. The field burning of agricultural waste and fuel wood burning are known to produce aerosol particles and trace gases that play important roles in atmospheric chemistry and climate changes (Levine et al., 1995).

Although studies on stable carbon and nitrogen isotope ratios of aerosols have been reported from several sites, little is known in Africa and no extensive studies have been conducted on $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ simultaneously (Billmarka et al., 2005; Rommerskirchen et al., 2006; Vogts et al., 2009). Further, the relation of nitrate and ammonium ions

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to total aerosol nitrogen has not been studied in Africa, although they could provide additional information on the source types of aerosols (e.g., Kundu et al., 2010a; Pavuluri et al., 2010).

In this paper, we present the measurement results on stable carbon and nitrogen isotopic composition in the ambient aerosols collected at a rural background site in Tanzania during an intensive field campaign carried out in May through August 2011. Here, we report the concentrations of total carbon (TC) and total nitrogen (TN) and their isotopic composition to better understand their potential sources. Southern African savanna where Tanzania locates is an important source region of biomass burning and long-range atmospheric transport of aerosols on a local and global scale (Lajtha and Marshall, 1994). This study provides for the first time baseline data sets of stable C and N isotopic composition of atmospheric aerosols from Tanzania, East Africa.

2. Experimental

2.1. Aerosol sampling

PM_{2.5} and PM₁₀ aerosol sampling was carried out at Solomon Mahlangu Campus of Sokoine University of Agriculture in Morogoro (06°47'40.8"S; 37°37'44.5"E, altitude 504 m, a.s.l.) from 30 May to 8 August 2011. This typical rural site (300 000 inhabitants) is located at about 200 km west of the coast of the Indian Ocean where the city of Dar es Salaam, a business capital in Tanzania, is located (Fig. 1). Aerosol samples were collected using PM_{2.5} and PM₁₀ low-volume filter samplers operated in parallel; one of the samplers was equipped with a Rupprecht and

Pataschnick PM_{2.5} inlet and the other with a Gent PM₁₀ inlet (Hopke et al., 1997). Samplers were placed at a meteorological synoptic station on campus, and aerosol collections were made at 2.7 m above ground level.

Each sampler used NILU stacked filter unit (SFU) cassettes, in which the front and back quartz fibre filters (Pallflex 2500QAT-UP, 47 mm) were placed in series. The samplers operated at a flow rate of 17 L/minute. The quartz filters were pre-baked at 450°C for 4 hours in a furnace to eliminate adsorbed organics before use. The two quartz fibre filters (front and back) in the PM_{2.5} inlet and PM₁₀ filter holder were intended to assess the extent of the artefacts. Quartz fibre filters can adsorb volatile organic compounds (VOCs) causing positive artefacts when measuring the PM. On the other hand, semi-volatile organic compounds (SVOCs) in aerosols may partially evaporate during sampling resulting in negative artefacts (Turpin et al., 2000; Hitznerberger et al., 2004). The PM mass and organic species (e.g., TC) determined on the back quartz filters were insignificant and therefore in this study the data from the front filter were adopted.

During the campaign, a total of 21 sets of samples and two field blanks for each of the PM_{2.5} and PM₁₀ samplers were collected on an approximately 24-hour basis and exchange of filters was performed at 7:30 am. Before and after sampling, quartz 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 Institute of Low Temperature Science, Hokkaido University and stored in a freezer at −20°C prior to analysis. All procedures were strictly quality-controlled to avoid any possible contamination of the samples.

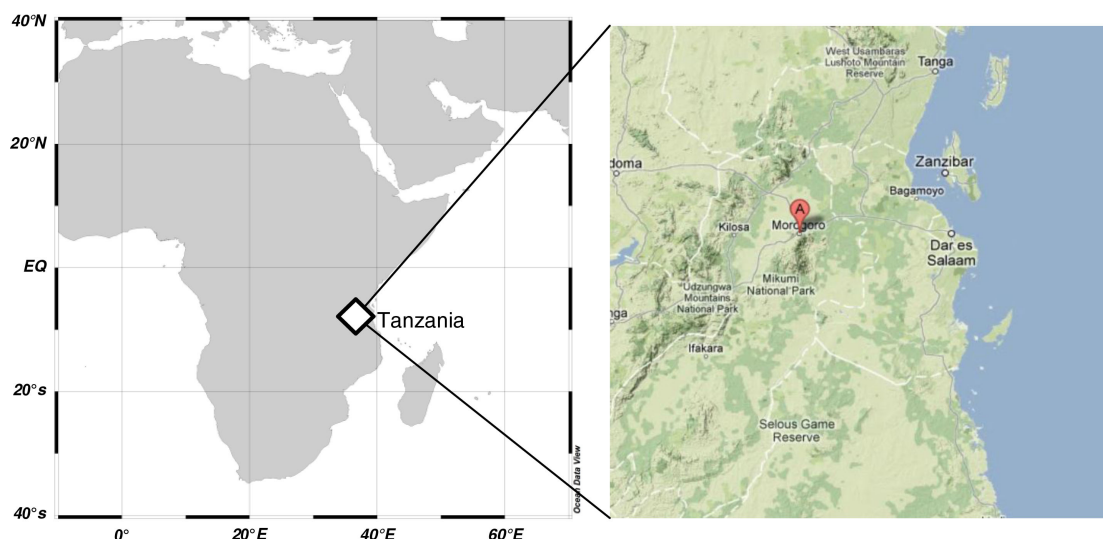


Fig. 1. Map showing the location of the sampling site of Morogoro, Tanzania.

2.2. Aerosol analysis

For the measurements of TC and TN contents and their isotopic compositions, a punch (1.54 cm²) of each quartz filter sample was cut off and used. The filter punch was rounded using a pair of flat tipped tweezers, placed into a tin cup and then caked into a ball. Before use, the tin cup was cleaned with acetone under ultrasonication to remove organic and other contaminants. The samples (filter plus tin cup) were then analysed for TC and TN and their isotopic compositions using elemental analyser (EA; model Carlo Erba NA 1500) and EA/isotope ratio mass spectrometer (IRMS) (Finnigan MAT Delta Plus) (Narukawa et al., 1999; Kawamura et al., 2004). Isotope data reported as $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values were defined as:

$$\delta^{13}\text{C} (\text{‰}) = \left[\left(\frac{^{13}\text{C}/^{12}\text{C}}{^{13}\text{C}/^{12}\text{C}} \right)_{\text{sample}} / \left(\frac{^{13}\text{C}/^{12}\text{C}}{^{13}\text{C}/^{12}\text{C}} \right)_{\text{standard}} - 1 \right] \times 1000 \quad (1)$$

$$\delta^{15}\text{N} (\text{‰}) = \left[\left(\frac{^{15}\text{N}/^{14}\text{N}}{^{15}\text{N}/^{14}\text{N}} \right)_{\text{sample}} / \left(\frac{^{15}\text{N}/^{14}\text{N}}{^{15}\text{N}/^{14}\text{N}} \right)_{\text{standard}} - 1 \right] \times 1000 \quad (2)$$

Before running the real samples for the determination of TC, TN, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ratios, we checked the instrument conditions with an empty tin cup three times and also evaluated a five-point calibration curve using acetanilide standard with the procedural blanks. The replicate analyses were not conducted due to the small size of actual sample filters. The analytical errors for $\delta^{13}\text{C}$ measurement based on repeated analyses of atmospheric aerosol samples at our laboratory were within 0.2‰ and those for $\delta^{15}\text{N}$ are 0.3‰ (Kawamura et al., 2004). We confirmed the similar analytical errors by running the authentic standards (acetanilide). TC and TN contents reported here were corrected for the field blanks, whose levels are <1.4% of actual samples. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values were also corrected for the field blanks using an isotopic mass balance equation. Details for the measurement of LG and water-soluble inorganic ions can be found in Mkoma et al. (2013), and a nonparametric correlation test (Spearman test) was applied to our data sets to explain the relationship between variables.

2.3. Meteorology

Meteorological parameters including precipitation, ambient temperature and relative humidity were recorded at a meteorological synoptic station at sampling site during sampling days. The prominent wind pattern during the sampling period was characterized by the southeasterly (SE) monsoons with daily average wind speed of 7.8 m s⁻¹. The average ambient temperature was 25°C with a range of 22–29°C. The daily average relative humidity ranged from 65 to 96% in the morning hours and from 41 to 60% in the

afternoon. Generally, aerosol sampling was mostly conducted on days with no rain and/or a very weak rain.

2.4. Air mass backward trajectories

In order to identify the source regions, backward air mass trajectories at arrival level of 500 m above the ground were computed using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model of the NOAA/ARL (<http://ready.arl.noaa.gov/HYSPLIT.php>; Draxler and Rolph, 2012). The isentropic backward 5-d air mass back trajectories for 24-hour samples indicated that the sampling site in Morogoro was mainly influenced by air masses from the Indian Ocean with mixtures of continental origins over Madagascar, through Mozambique and Tanzania (Fig. 2).

3. Results and discussion

3.1. Total aerosol mass, TC, TN, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and TC/TN and TC/PM ratios

The variations of PM_{2.5} and PM₁₀ aerosol mass concentrations are shown in Fig. 3. Mean aerosol mass concentrations for PM_{2.5} and associated standard deviation were $33.4 \pm 9.7 \mu\text{g m}^{-3}$ (range: 16.6–61.3 $\mu\text{g m}^{-3}$), whereas those of PM₁₀ were $54.2 \pm 16.1 \mu\text{g m}^{-3}$ (range: 35.7–99.5 $\mu\text{g m}^{-3}$). The aerosol mass concentration levels obtained here are comparable to or lower than the previous studies from Morogoro (Mkoma et al., 2009a, b). The mean PM mass back/front filter ratios from the quartz fibre filters for the PM_{2.5} and PM₁₀ during sampling period were determined. On average, 7–16% of the PM mass on the front filters for the two size fractions was due to sampling artefacts. The artefacts are thought to be mostly positive, i.e., due to adsorption of VOCs and of volatile inorganic species (Turpin et al., 2000; Hitznerberger et al., 2004). In previous 2005 and 2006 campaigns at Morogoro on average 9 to 13% of the PM mass were due to sampling artefacts (Mkoma et al., 2010).

Concentrations of TC and TN in PM_{2.5} and PM₁₀ are presented in Tables 1 and 2, respectively. TC contents ranged from 3.1 to 10.4 $\mu\text{g m}^{-3}$ (mean: $6.5 \pm 2.1 \mu\text{g m}^{-3}$) in PM_{2.5}, whereas those of PM₁₀ were 4.2–18.0 (mean: $9.2 \pm 3.5 \mu\text{g m}^{-3}$). On average, TC accounted for 20.8% (range: 9.6–34.7%) of PM_{2.5} and 17% (range: 11.8–28.7%) of PM₁₀ mass. These results show elevated concentrations of TC in months of July–August, suggesting enhanced biomass/biofuel burning activities and contributions of primary biogenic particles (mostly in PM₁₀ fraction). Domestic use of fuel wood and charcoal, which are common in Tanzania, could also contribute to the observed levels of TC at our sampling site.

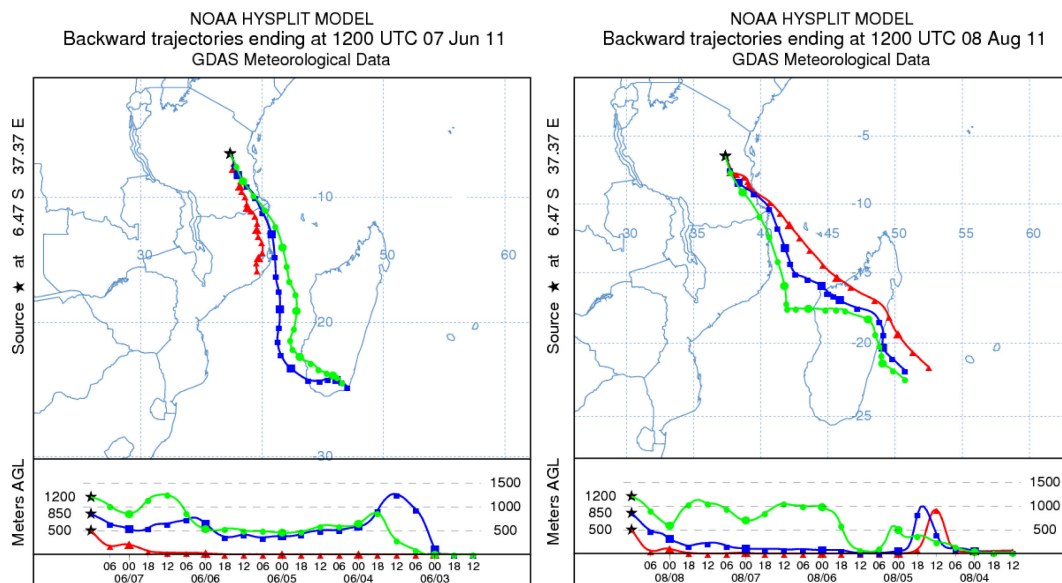


Fig. 2. Typical examples of 5-day backward air mass trajectories arriving at Morogoro during the May–August 2011 sampling period.

The mean percentage of PM_{10} carbon (or nitrogen) that is actually $\text{PM}_{2.5}$ and which fraction is coarse were calculated for the campaign on the basis of the data for $\text{PM}_{2.5}$ and PM_{10} samples taken in parallel and then averaged over all samples from the campaign. The mean $\text{PM}_{2.5}/\text{PM}_{10}$ carbon ratios were $68 \pm 19\%$ (range: 34%–98%). The results indicate that most of PM_{10} carbon was mainly in fine ($\text{PM}_{2.5}$) fraction during the campaign. The possible main contributors to carbon are biomass burning particles and secondary aerosol, both of which are known to be preferentially associated with $\text{PM}_{2.5}$ fraction (Fuzzi et al., 2007). In contrast, a small contribution from soil dust may be associated with coarse particles.

$\delta^{13}\text{C}$ of TC ranged from -26.1 to -20.6‰ in $\text{PM}_{2.5}$ and -24.4 to -22.4‰ in PM_{10} with a mean of -23.6‰ in both fractions (Table 1 and 2). We found substantially

higher $\delta^{13}\text{C}$ values in $\text{PM}_{2.5}$ samples, suggesting that biomass burning of C_4 plants dominated in savanna grasses occasionally contributes to the formation of organic aerosols in the region (Rommerskirchen et al., 2006). The high range for $\delta^{13}\text{C}$ observed in PM_{10} may be influenced by soil dust contributions and biogenic emissions of plant waxes.

The isotopic mass balance eqs. (3) and (4) were used to calculate the isotope ratios of fine ($\text{PM}_{2.5}$) and coarse ($\text{PM}_{10}-\text{PM}_{2.5}$) particles (Kawamura and Watanabe, 2004).

$$\delta^{13}\text{C}_{\text{coarse}} = [\delta^{13}\text{C}(\text{PM}_{10}) - F_{\text{fine}} \times \delta^{13}\text{C}_{\text{fine}}] / F_{\text{coarse}} \quad (3)$$

$$\delta^{15}\text{N}_{\text{coarse}} = [\delta^{15}\text{N}(\text{PM}_{10}) - F_{\text{fine}} \times \delta^{15}\text{N}_{\text{fine}}] / F_{\text{coarse}} \quad (4)$$

where $\delta^{13}\text{C}_{\text{coarse}}$ and $\delta^{15}\text{N}_{\text{coarse}}$, and $\delta^{13}\text{C}_{\text{fine}}$ and $\delta^{15}\text{N}_{\text{fine}}$ are isotopic composition of (C and N) coarse and fine

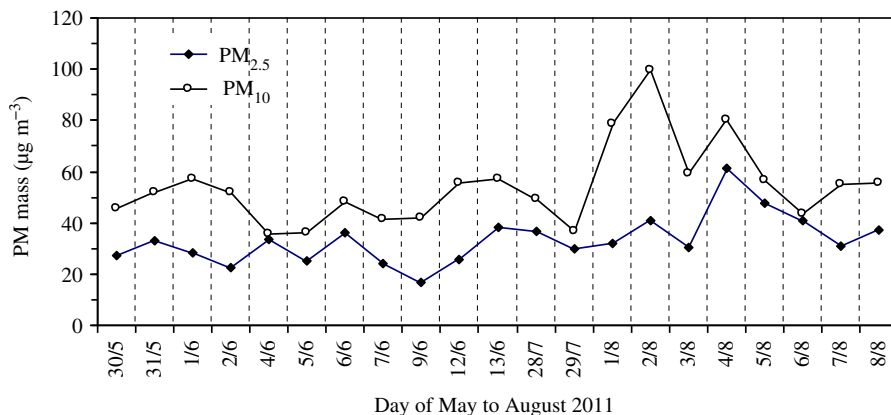


Fig. 3. Trends of aerosol mass concentrations ($\mu\text{g m}^{-3}$) in $\text{PM}_{2.5}$ and PM_{10} during the May–August 2011 sampling period at Morogoro.

Table 1. Concentrations of TC and TN ($\mu\text{g m}^{-3}$), their isotope ratios (‰), TC/TN and TC/PM (%) in PM_{2.5} from Morogoro, Tanzania ($n = 21$)

Date	$\delta^{13}\text{C}$	$\delta^{15}\text{N}$	TC	TN	TC/TN	TC/PM	TN/PM
30/5/2011	−25.4	NA	6.1	BDL	NA	22.4	NA
31/5/2011	−25.8	16.1	7.2	0.5	13.9	21.8	1.6
1/6/2011	−25.1	13.5	3.7	0.6	6.3	12.9	2.0
2/6/2011	−25.9	NA	6.0	BDL	NA	26.4	NA
4/6/2011	−24.8	13.4	3.9	0.4	10.4	11.6	1.1
5/6/2011	−24.3	15.3	4.5	0.4	11.5	17.8	1.6
6/6/2011	−25.6	NA	7.4	BDL	NA	20.3	NA
7/6/2011	−25.6	14.1	5.3	0.4	12.8	22.1	1.7
9/6/2011	−26.1	NA	3.1	BDL	NA	19.0	NA
12/6/2011	NA	NA	4.5	BDL	NA	17.5	NA
13/6/2011	NA	NA	7.9	0.6	13.7	20.6	1.5
28/7/2011	−22.6	20.3	8.0	0.9	9.2	21.9	2.4
29/7/2011	−22.0	13.5	10.4	1.4	7.6	34.7	4.6
1/8/2011	−21.8	22.1	9.7	0.9	11.4	30.0	2.6
2/8/2011	−20.6	17.2	9.7	1.5	6.3	23.7	3.8
3/8/2011	−21.2	17.9	8.3	0.6	12.8	27.3	2.1
4/8/2011	NA	NA	6.6	0.7	10.2	10.8	1.1
5/8/2011	−22.4	14.2	6.9	0.7	9.6	14.5	1.5
6/8/2011	−21.3	NA	4.2	BDL	NA	9.6	NA
7/8/2011	−21.7	16.4	5.5	0.7	8.1	17.5	2.2
8/8/2011	−21.8	16.8	7.7	0.6	13.5	20.8	1.5
Mean $\pm$ SD	−23.6 $\pm$ 1.9	16.2 $\pm$ 2.7	6.5 $\pm$ 2.1	0.7 $\pm$ 0.3	10.5 $\pm$ 2.6	20.8 $\pm$ 6.4	2.2 $\pm$ 1.0

BDL: below detection limit, DL: ca. $0.02 \mu\text{g m}^{-3}$ for TC and $0.05 \mu\text{g m}^{-3}$ for TN. NA: not available.

particles, respectively. F_{fine} is a fraction of fine particles, whereas F_{coarse} is a fraction of coarse particles ($F_{\text{fine}} + F_{\text{coarse}} = 1$).

Table 3 shows the results of isotopic compositions of C and N in the fine and coarse fractions during 2011 wet and dry season samplings. During dry season (28 July to 8 August), fine particles are more enriched with ^{13}C , suggesting more contribution from the burning of C_4 plants (they have evolved in the dry conditions in the history of plants) than coarse particles. C_4 plants are probably more active when weather is dried in East Africa. However, in the wet season (30 May to 13 June), $\delta^{13}\text{C}$ of coarse particles showed higher ratios than fine particles. Although it is difficult to explain the reason, we consider that there is some unknown process behind the result.

TN contents had a narrow range of $0.4\text{--}1.6 \mu\text{g N m}^{-3}$ (mean: $0.7 \pm 0.3 \mu\text{g N m}^{-3}$) in PM_{2.5} and $0.6\text{--}1.6 \mu\text{g N m}^{-3}$ (mean: $0.8 \pm 0.2 \mu\text{g N m}^{-3}$) in PM₁₀. TN comprised of $1.1\text{--}4.6\%$ (mean: 2.2%) of PM_{2.5} and $1.1\text{--}2.6\%$ (mean: 1.6%) of PM₁₀ mass. Variations of TN may be due to the wet scavenging (most N species are water-soluble) and the differences in photochemical atmospheric processes. The calculated mean percentage ratio of PM_{2.5} to PM₁₀ nitrogen during the campaign was $72 \pm 14\%$ ranging from 57 to 98%. The ratios indicate that most of nitrogen was mainly present in fine (PM_{2.5}) fraction and possibly associated with

biomass/biofuel burning activities and secondary aerosols. TC/TN weight ratios range from 6.3 to 13.9 in PM_{2.5} and from 6.9 to 14.1 in PM₁₀ (Table 1 and 2). The higher C/N ratios suggest more contributions of organic aerosols from biomass/biofuel burning in East Africa. A strong positive correlation ($r^2 > 0.88$, $p < 0.001$) between TC and TN in PM₁₀ (Fig. not shown here) may indicate that TC and TN have a common source. We also found strong correlations ($r^2 > 0.70$) between PM₁₀ mass and TC ($p < 0.001$) or TN ($p < 0.05$) (Fig. not shown here).

$\delta^{15}\text{N}$ of TN in PM_{2.5} ranged from $+13.4$ to $+22.1\%$ (mean: $+16.2 \pm 2.7\%$), whereas those of PM₁₀ are slightly lower ranging from $+10.5$ to $+18.7\%$ (mean: $+13.7 \pm 2.2\%$) (Tables 1 and 2). The isotopic compositions of N in the fine and coarse fractions of Morogoro during wet and dry season campaigns are given in Table 3. The $\delta^{15}\text{N}$ showed higher ratios in fine particles than coarse particles in both wet and dry season. These results suggest that enrichment of ^{15}N in fine particles is more important than coarse particles in both seasons. The higher $\delta^{15}\text{N}$ ratios in dry season further indicate that isotopic enrichment of ^{15}N in the aerosols is more significant in dry season due to partitioning reaction between gas (NH_3) and particle $[(\text{NH}_4)_2\text{SO}_4]$ (Pavuluri et al., 2010). $\delta^{15}\text{N}$ variability at our site could also be controlled by biomass burning activities, and by nitrogenous species (e.g., NH_3)

Table 2. Concentrations of TC and TN ($\mu\text{g m}^{-3}$), their isotope ratios (‰), TC/TN and TC/PM (‰) in PM_{10} from Morogoro, Tanzania ($n = 21$)

Date	$\delta^{13}\text{C}$	$\delta^{15}\text{N}$	TC	TN	TC/TN	TC/PM	TN/PM
30/5/2011	−24.0	10.4	6.0	0.7	9.2	13.3	1.4
31/5/2011	−24.1	11.6	8.2	0.7	11.0	ND	NA
1/6/2011	−24.4	NA	6.8	BDL	NA	11.8	NA
2/6/2011	−24.4	NA	8.3	BDL	NA	16.1	NA
4/6/2011	−23.4	13.0	4.2	0.6	6.9	11.8	1.7
5/6/2011	−23.0	12.9	6.4	0.7	9.3	17.7	1.9
6/6/2011	−23.7	12.7	9.7	0.8	12.0	20.1	1.7
7/6/2011	−23.9	13.4	7.5	0.7	10.3	18.2	1.8
9/6/2011	−23.8	10.7	6.4	0.7	8.7	15.2	1.8
12/6/2011	−23.8	11.2	9.3	0.8	11.6	16.8	1.4
13/6/2011	−23.4	15.4	11.4	1.0	11.9	19.9	1.7
28/7/2011	−23.9	13.4	5.9	0.6	10.2	12.0	1.2
29/7/2011	−23.5	16.5	10.5	0.9	11.1	28.7	2.6
1/8/2011	−22.7	17.0	16.0	1.2	13.2	20.3	1.5
2/8/2011	−22.6	18.7	18.0	1.6	11.4	18.1	1.6
3/8/2011	−22.4	14.6	12.6	0.9	14.1	21.3	1.5
4/8/2011	−23.9	NA	11.7	BDL	NA	14.6	NA
5/8/2011	−23.8	12.9	8.8	0.8	11.2	15.5	1.4
6/8/2011	−23.7	13.9	5.3	0.5	11.5	12.2	1.1
7/8/2011	NA	NA	9.8	0.8	12.1	17.8	1.5
8/8/2011	−23.4	14.7	11.2	0.8	14.1	20.1	1.4
Mean $\pm$ SD	−23.6 $\pm$ 0.5	13.7 $\pm$ 2.2	9.2 $\pm$ 3.5	0.8 $\pm$ 0.2	11.1 $\pm$ 1.8	17.0 $\pm$ 4.2	1.6 $\pm$ 0.3

BDL: below detection limit, DL: ca. $0.02 \mu\text{g m}^{-3}$ for TC and $0.05 \mu\text{g m}^{-3}$ for TN. NA: not available.

from agricultural sources, in particular cattle raising (Streets et al., 2003).

3.2. Temporal variations of TC, $\delta^{13}\text{C}$ and relations with biomass burning tracers

Temporal variations of TC and its isotope ratio ($\delta^{13}\text{C}$) for $\text{PM}_{2.5}$ and PM_{10} are shown in Fig. 4. The highest TC contents were observed between 29 July and 2 August for $\text{PM}_{2.5}$ and 2–3 August for PM_{10} . The elevated TC concentrations can be associated with the enhanced source strength of local and regional biomass burning activities. In spite of variable concentrations of TC ($3.1\text{--}18.0 \mu\text{g m}^{-3}$) and LG ($0.038\text{--}0.659 \mu\text{g m}^{-3}$, data from Mkoma et al., 2013), LG/TC ratios (on carbon basis) did not show a significant difference between $\text{PM}_{2.5}$ (mean:

0.029, range: 0.009–0.042) and PM_{10} (mean: 0.027, range: 0.012–0.039).

Figure 5 shows strong positive correlations between TC and LG ($p < 0.001$) in both $\text{PM}_{2.5}$ and PM_{10} and nss-K^+ ($p < 0.05$ in $\text{PM}_{2.5}$ and $p < 0.001$ in PM_{10}) suggesting an important contribution to TC from biomass/biofuel burning emissions from residential wood burning and charcoal-making operations in East Africa. The non-sea-salt (nss-K^+) was calculated using Na^+ as a reference tracer for sea-salt and obtained by subtracting the sea-salt contribution from the measured K^+ data sets (Riley and Chester, 1971). The intercepts of the least square fit are all positive on TC axis, implying that in addition to biomass burning there is a contribution to TC either from direct emission of bioaerosols from plants or from secondary formation of organic aerosols from biogenic VOCs.

Table 3. Isotope ratios (‰) of carbon and nitrogen in the fine and coarse fractions of Morogoro, Tanzania, during 2011 wet and dry season campaigns

	Wet season		Dry season		Wet season		Dry season	
	$\delta^{13}\text{C}_{\text{fine}}$	$\delta^{13}\text{C}_{\text{coarse}}$	$\delta^{13}\text{C}_{\text{fine}}$	$\delta^{13}\text{C}_{\text{coarse}}$	$\delta^{15}\text{N}_{\text{fine}}$	$\delta^{15}\text{N}_{\text{coarse}}$	$\delta^{15}\text{N}_{\text{fine}}$	$\delta^{15}\text{N}_{\text{coarse}}$
Min.	−26.1	−23.8	−22.6	−30.8	13.4	7.1	13.5	5.8
Max.	−24.3	−17.8	−20.6	−23.4	16.1	12.5	22.1	19.7
Mean $\pm$ SD	−25.4 $\pm$ 0.6	−21.5 $\pm$ 2.1	−21.7 $\pm$ 0.7	−26.5 $\pm$ 3.0	14.7 $\pm$ 1.2	9.1 $\pm$ 2.9	17.4 $\pm$ 3.1	12.1 $\pm$ 5.1

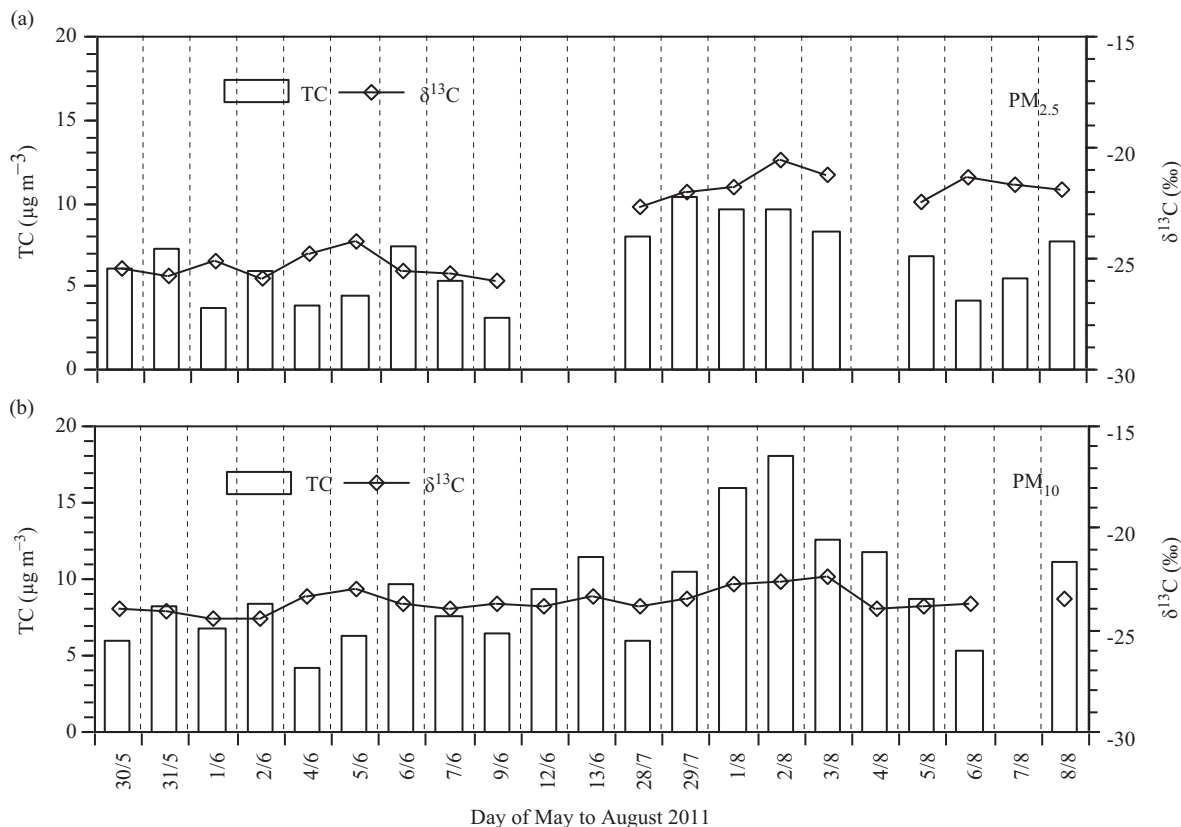


Fig. 4. Temporal variation of TC and $\delta^{13}\text{C}$ in (a) $\text{PM}_{2.5}$ and (b) PM_{10} during the May–August 2011 sampling period at Morogoro.

The background TC concentrations in $\text{PM}_{2.5}$ and PM_{10} (Fig. 4) could be involved with emissions from soil dust and biogenic sources (nss- K^+ can be emitted from biogenic debris and soil dust). The weak correlation observed between TC and nss- K^+ in $\text{PM}_{2.5}$ (Fig. 5a) could be associated with secondary organic aerosols (high temperature and most organic compounds are water-soluble). Use of wood and charcoal for domestic cooking and heating is common in Tanzania, which is enhanced in months of March through May.

On the other hand, Na^+/TC ratio in the marine aerosols was reported to be 2.3 (Cavalli et al., 2004) and its relation to $\delta^{13}\text{C}$ of TC is used to understand the relative contribution of seawater organics to marine aerosols (Narukawa et al., 2008). Our average Na^+/TC ratio was 0.18, and no correlation was found between $\delta^{13}\text{C}$ with Na^+/TC ratios and even with NO_3^- (Fig. not shown). This suggests that the influence of sea-salt particles to our site is less important.

The $\delta^{13}\text{C}$ was poorly correlated with TC in $\text{PM}_{2.5}$ ($r^2=0.22$), but somewhat good correlation was obtained for PM_{10} ($r^2=0.37$) (Fig. not shown here). The correlation between $\delta^{13}\text{C}$ and TC may indicate possible emissions of soil dust and biological particles and a possible condensation of volatile and semi-volatile organics derived from biomass burning of C_4 plants on pre-existing particles.

3.3. Temporal variations in TN, $\delta^{15}\text{N}$ and contributions of N species to TN

Figure 6 shows temporal variations of TN and $\delta^{15}\text{N}$ for $\text{PM}_{2.5}$ and PM_{10} . TN contents in $\text{PM}_{2.5}$ show high levels on 29 July and 2 August, whereas the levels in PM_{10} show a gradual increase during sampling period with highest values on 1–2 August. On the other hand, $\delta^{15}\text{N}$ showed higher values on 2 August in both fractions. The relationships among biomass burning tracers (nss- K^+ and LG, hereafter abbreviated as LG), TN and $\delta^{15}\text{N}$ were examined (Fig. not shown here). TN showed good correlation with nss- K^+ ($r^2=0.63$, $p<0.001$ in $\text{PM}_{2.5}$ and $r^2=0.55$, $p<0.001$ in PM_{10}) and LG ($r^2=0.33$, $p<0.05$ in $\text{PM}_{2.5}$ and $r^2=0.42$, $p<0.001$ in PM_{10}). In contrast, $\delta^{15}\text{N}$ showed poor correlation with nss- K^+ ($r^2=0.33$) and LG ($r^2=0.14$) in $\text{PM}_{2.5}$ but showed good correlation with nss- K^+ ($r^2=0.67$, $p<0.001$) and LG ($r^2=0.51$, $p<0.05$) in PM_{10} . The NH_4^+ and NO_3^- , which are important constituents of TN (Pavuluri et al., 2010), may have been enhanced in those days from local sources possibly by gas-to-particle conversion of NH_3 and NO_x (secondary formation).

Variabilities of $\delta^{15}\text{N}$ for both sizes ($\text{PM}_{2.5}$ and PM_{10}) were larger than those of $\delta^{13}\text{C}$. These variations may be

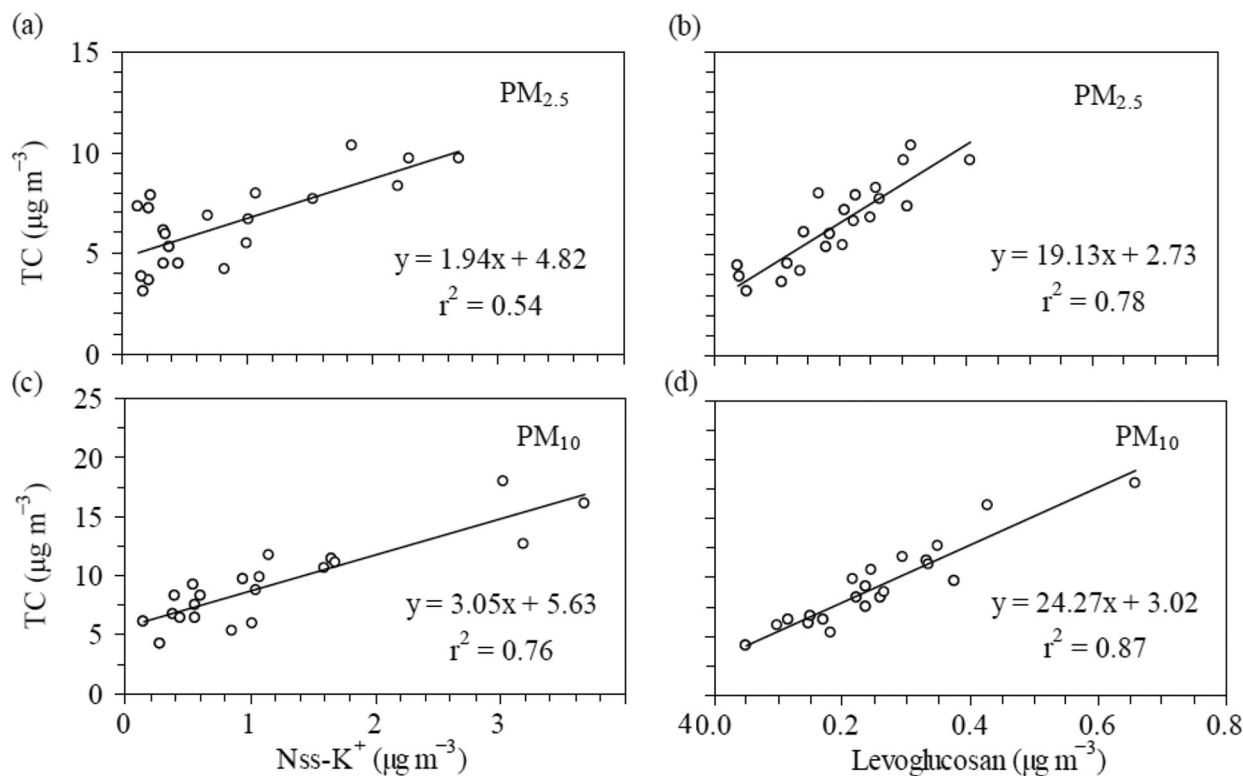


Fig. 5. Relation between TC with levoglucosan and nss- K^+ in $PM_{2.5}$ (a, b) and PM_{10} (c, d) during the sampling period.

due to changes in the contribution of local sources and secondary formation pathways of nitrogen aerosols (Widory, 2007; Pavuluri et al., 2010). However, larger $\delta^{15}N$ values for PM_{10} in July–August 2011 may have originated from soil dust in addition to the influence of biomass burning activities (Turekian et al., 1998), being supported by good correlation ($r^2=0.62$) between $\delta^{15}N$ and Ca^{2+} (crustal element) for PM_{10} in same period. It is important to note that our site is neither influenced by fossil fuel combustion products that are less enriched with ^{15}N ($\delta^{15}N < 0\text{‰}$) (Widory, 2007), nor contributed by particulate nitrogen from marine emissions; $\delta^{15}N$ did not correlate with Na^+/TN ratios. Hence, relatively high $\delta^{15}N$ ratios obtained in the present aerosol samples could not be explained by the influence of marine aerosols and anthropogenic activities.

The contributions of inorganic-N species (NH_4^+ and NO_3^-) to TN (inorganic plus organic-N) measured by EA were calculated. NH_4^+ was found to account on average for 62.5% of TN (range: 20.9–88.7%) in $PM_{2.5}$ and 34.4% (range: 7.9–85.0%) in PM_{10} , whereas NO_3^- comprised on average of 4.1% (range: 2.8–8.8%) and 8.0% (range: 3.5–17.5%) in $PM_{2.5}$ and PM_{10} , respectively. Higher contribution of NH_4^+ to TN than NO_3^- may indicate a strong NH_3 emission from biomass burning, cattle (livestock) farms, open sewage and landfills (Sutton et al.,

2000). Outflow of domestic sewage systems and dumping of solid waste into open landfills are common in Tanzania. On the other hand, the global nitrogen contributions from animal manure have been estimated to be between 40 and 60% for NH_4^+ and below 10% for NO_x (Oenema and Tamminga, 2005). Figure 7 shows relations between NH_4^+ , NO_3^- , NH_4^+ plus NO_3^- , and TN in $PM_{2.5}$ and PM_{10} . Strong positive correlations ($p < 0.001$ in $PM_{2.5}$ and $p < 0.05$ in PM_{10}) suggest that significant portion of TN was mainly composed of NH_4^+ and, to lesser extent, NO_3^- , indicating that organic nitrogen (non-water soluble) is less important in the Morogoro aerosols. NH_3 from biomass burning is less enriched with ^{15}N (Turekian et al., 1998).

A good correlation was obtained for both $PM_{2.5}$ and PM_{10} between $\delta^{15}N$ and TN during sampling period ($r^2=0.59$ and $r^2=0.57$, $p < 0.05$), respectively (Fig. not shown). These correlations may suggest a presence of different forms of nitrogen and/or larger $\delta^{15}N$ ratios in aerosols. Also, a good correlation of $\delta^{15}N$ with TN may be associated with isotopic enrichment of ^{15}N during exchange and portioning reactions of gaseous and particulate nitrogen species (e.g., NH_3 and NH_4^+), causing a enrichment of ^{15}N in aerosol nitrogen (Kundu et al., 2010a; Pavuluri et al., 2010).

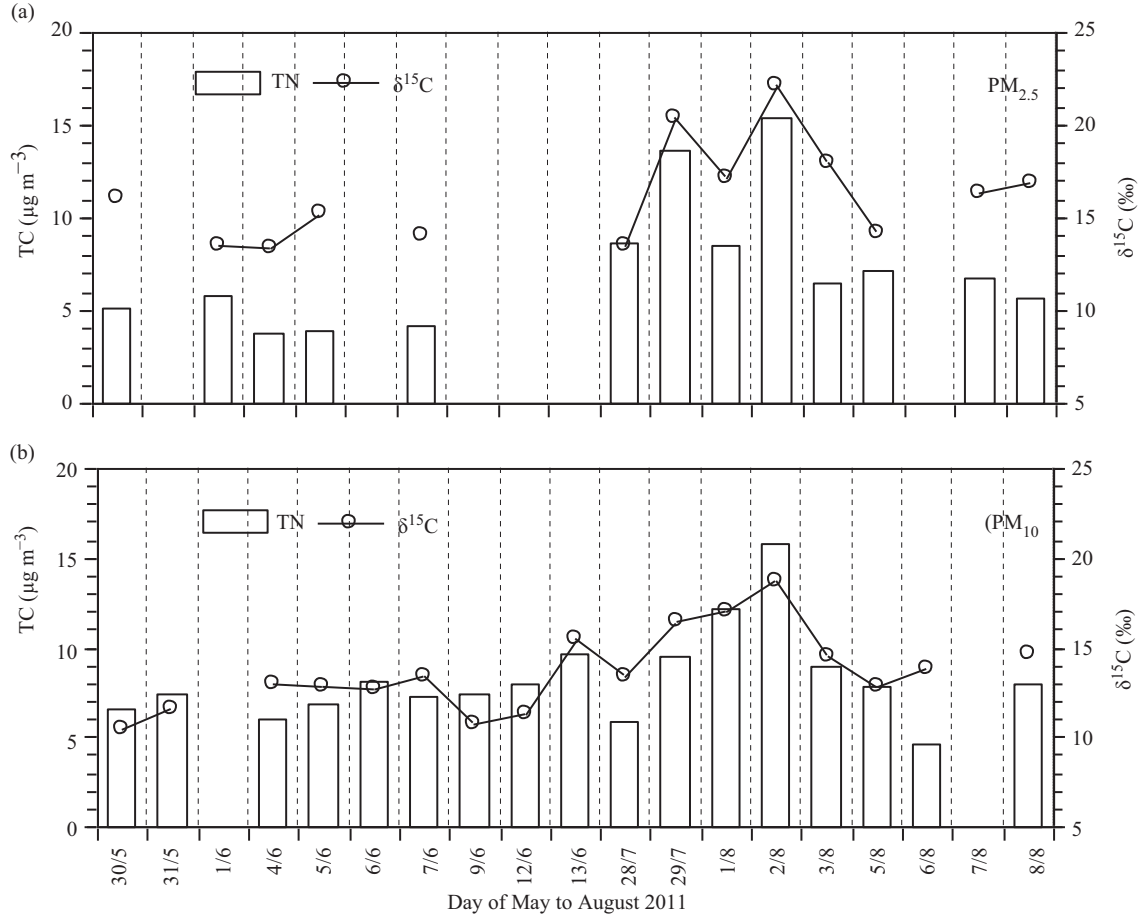


Fig. 6. Temporal variation of TN and $\delta^{15}\text{N}$ in (a) $\text{PM}_{2.5}$ and (b) PM_{10} during the May–August 2011 sampling period at Morogoro.

3.4. Comparisons of TC, TN, and their isotopic ratios with other studies

Concentrations of TC, TN, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in Tanzania (Tables 1 and 2) are compared with those reported from Africa and other sites around the world. Mean TC/aerosol mass ratios in Tanzania are 19.1–21.1% in $\text{PM}_{2.5}$ and 16.1–18.1% in PM_{10} . TC contents from our site are comparable to or lower than those ($1.6\text{--}46.4\text{ }\mu\text{g m}^{-3}$) reported in tropical aerosols from the Ivory Coast in West Africa (Cachier et al., 1985) and those ($14.0\text{--}55.0\text{ }\mu\text{g m}^{-3}$) from central Africa (Ruellan et al., 1999).

We found higher values of $\delta^{13}\text{C}$ of TC in $\text{PM}_{2.5}$ during the July and August 2011 period. Aerosol studies in the Ivory Coast and Burkina Faso (West Africa) reported larger $\delta^{13}\text{C}$ in similar months when the contribution of C_4 plants sources to the atmospheric aerosols was dominant (Cachier et al., 1985). Studies from the Amazon basin in Brazil, where influence of biomass burning is significant, showed average $\delta^{13}\text{C}$ value of $-25.8 \pm 0.5\text{‰}$ (range: -26.9 to -24.9‰) in Santarém, Pará State, which is an area dominated with C_3 plants (Martinelli et al., 2002),

and average $\delta^{13}\text{C}$ value of -24.7‰ (range: -26.1 to -23.5‰) in Rondônia (Kundu et al., 2010b). Hence, it is likely that possible sources of organic aerosols over our sampling site could be regional biomass burning of C_3 and C_4 plants (Gelencsér, 2004; Rommerskirchen et al. 2006; Vogts et al., 2009).

On the other hand, the C/N ratios ($6.3\text{--}13.9$ in $\text{PM}_{2.5}$ and $6.9\text{--}14.1$ in PM_{10}) found in Tanzania are much higher than those reported in aerosols from India and Korea (Pavuluri et al., 2010; Jung and Kawamura, 2011), whereas $\delta^{15}\text{N}$ values are comparable to those (range: $+8.3$ to $+18.7\text{‰}$) from the Amazon basin (mean: $+11.5 \pm 2.1\text{‰}$) and Piracicaba, São Paulo, Brazil (mean: $+10.6 \pm 2.8\text{‰}$), regions that are significantly influenced by biomass (C_3 and C_4 plants) burning (Martinelli et al., 2002).

3.5. Contribution from burning of C_3 and C_4 plants to aerosol particles

Biomass and biofuel combustion is common in both rural and urban areas in southern African countries including

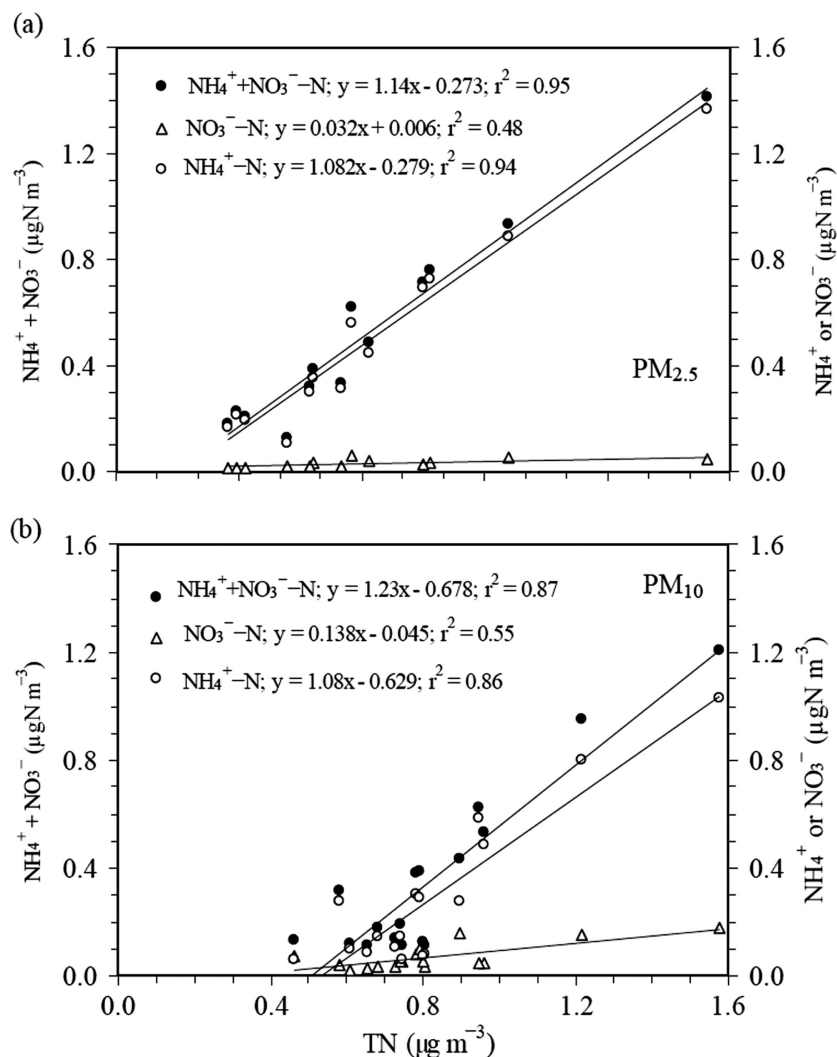


Fig. 7. Relation between NO_3^- -N, NH_4^+ -N and $(\text{NH}_4^+ + \text{NO}_3^-)$ -N with TN in (a) PM_{2.5} and (b) PM₁₀ during the sampling period.

Tanzania. Use of wood and charcoal for domestic cooking and heating in Tanzania is enhanced in wet season (March to June), whereas field burning of agriculture residues, charcoal-making operations and forest/wild fires which cover small areas and a short duration occur in dry season (July to October) (Swap et al., 1996; Mkoma et al., 2009b). It is therefore likely that changes in $\delta^{13}\text{C}$ of TC can be modulated by biomass/biofuel burning activities including savanna fire events of southern African regions (Swap et al., 1996) and domestic wood burning.

The southern African aerosol studies based on stable carbon isotopic compositions suggest a predominant burning of C₃ plants (Lajtha and Marshall, 1994). Recent studies on land cover and cropland distribution reported that larger areas of East Africa where Tanzania locates are covered with C₃ and C₄ vegetation, which include tropical grasses, deciduous tropical forest, shrubs and woodlands

(Still et al., 2003; Rommerskirchen et al. 2006; Vogts et al. 2009). Most southern African countries are characterized by savanna ecosystems and the main vegetation types in Madagascar and Mozambique (possible source regions of air masses) are tropical forest, woodlands and shrubs (Arino et al., 2008). Land use change, especially the conversion of natural vegetation to cropland, can result in a range of environmental impacts including aerosol loading into the ambient atmosphere.

Further, Cachier et al. (1985) found larger $\delta^{13}\text{C}$ values for the aerosols in Africa during dry season months. Hence, it is very likely that contributions of C₄ plant burning to ambient aerosols in Tanzania are important during the sampling period. Because our sampling site is located in a typical rural area, contribution of anthropogenic TC from traffic should be minimal, whose $\delta^{13}\text{C}$ values range from -28 to -26‰ (Widory, 2006). The aerosol chemical mass

closure in previous study at Morogoro (Mkoma et al., 2009b) showed that elemental carbon (EC) was insignificant attributing only 1.9% of the gravimetric PM_{10} mass. It was mainly derived from charcoal-making process and field burning of agricultural residues (Mkoma et al., 2009b). Secondary organic aerosol formation from biogenic VOCs is assumed to be less significant than biomass/biofuel combustion in $PM_{2.5}$ (high temperature). Since our study has not been done near source site and lacks a representative emission factors for the region, we estimate relative contributions from the burning of C_3 plants ($\%C_3$) and C_4 plants ($\%C_4$) to TC based on stable carbon isotopic composition of TC as follows:

C_3 plants (%)

$$= \left[(\delta^{13}C)_{\text{aerosol}} - (\delta^{13}C)_{C_4} \right] / \left[(\delta^{13}C)_{C_3} - (\delta^{13}C)_{C_4} \right] \quad (5)$$

$$C_4 \text{ plants (\%)} = 1 - (\%C_3) \quad (6)$$

where $(\delta^{13}C)_{\text{aerosol}}$ is stable carbon isotopic composition of aerosol particles. $(\delta^{13}C)_{C_3}$ and $(\delta^{13}C)_{C_4}$ are isotope ratios of C_3 and C_4 plants, respectively, whose end members are assumed to be -30.5‰ and -13.5‰ based on average $\delta^{13}C$ determined for leaves of C_3 and C_4 vegetation (Martinelli et al., 2002).

Using eqs. 5 and 6, average contributions of burning C_3 plants to TC were 59% in both $PM_{2.5}$ (range: 42–74%) and PM_{10} (range: 39–64%). Conversely, average contributions

of C_4 plants were 41% in $PM_{2.5}$ (range: 26–58%) and PM_{10} (range: 36–61%). The main dominant crops in the eastern and southern Africa are maize, rice, sorghum, beans and wheat, which could significantly contribute to aerosols loading during the burning season of agricultural residue in addition to wild fires. Thus, both C_3 and C_4 plant residues are burned and the burning products should show different isotopic composition. In our study, we found strong positive correlation between $\delta^{13}C$ of TC with $nss-K^+$ ($r^2=0.64-0.72$) and weak correlations with LG ($r^2=0.31-0.32$) in both $PM_{2.5}$ and PM_{10} (Fig. 8a–d). These results indicate that the burning activities of C_3 and C_4 plants have a significant influence on organic aerosol composition (Fu et al., 2012) over Tanzania. We found active fire spots from MODIS satellite images in June to end of October (Fig. 9) in Madagascar, Mozambique and Tanzania where air masses mostly travelled through the region to our sampling site in Morogoro during our campaigns (http://earthobservatory.nasa.gov/GlobalMaps/view.php?d1=MOD14A1_M_FIRE).

Our results seem to be consistent with other studies, which indicate that contributions from the burning of C_3 and C_4 plants are dominant in Africa (Still et al., 2003; Rommerskirchen et al. 2006; Vogts et al. 2009). However, in the large land area that is covered by savanna vegetation, contribution of biomass burning from C_4 plants (e.g., grasses) to ambient aerosols could be large (Rommerskirchen

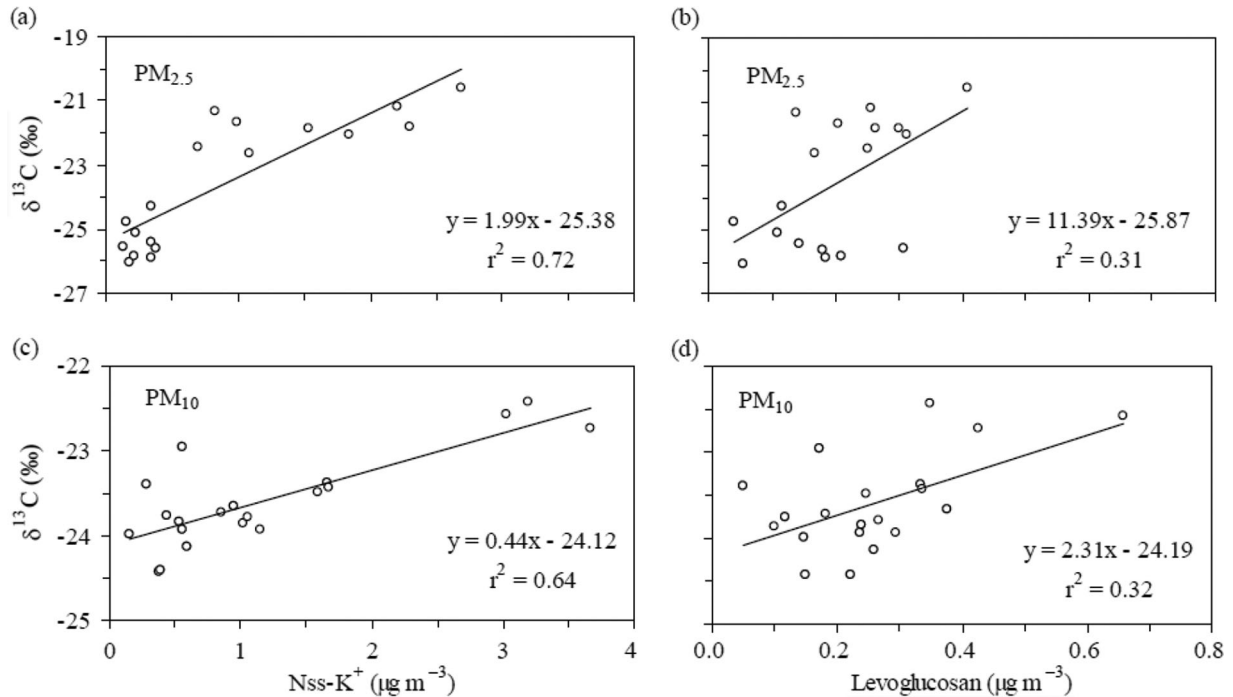


Fig. 8. Linear relation between $\delta^{13}C$ of TC with $nss-K^+$ and levoglucosan in (a, b) $PM_{2.5}$ and (c, d) PM_{10} during the sampling period in tropical aerosols from Tanzania.

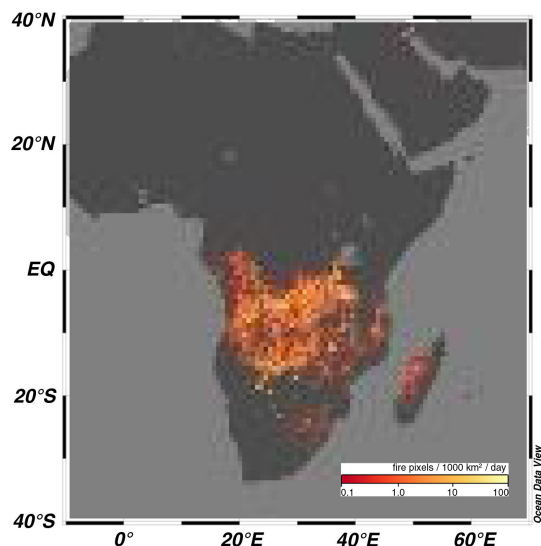


Fig. 9. Biomass burning active fire spots detected by MODIS satellite images (from NASA website) over southern and eastern Africa and Madagascar in July 2011.

et al. 2006). A study in Rondônia, Brazil, reported an average contribution of C_4 plants of 40% (range: 46–54%) (Kundu et al., 2010b). Also, Martinelli et al. (2002) reported a minimum and maximum contribution of C_4 plants to aerosol particles to be 45 and 62%, respectively, with a mean of 55% in Piracicaba, southeast of the Amazon basin in Brazil. Therefore, in Tanzania depending on size fraction of the aerosol particles, the contribution of C_3 and C_4 plants from biomass/biofuel burning is expected to be important.

4. Summary and conclusions

This study reports stable carbon and nitrogen isotopic composition of the atmospheric aerosols from Tanzania, East Africa. $\delta^{13}C$ of TC in $PM_{2.5}$ ranged from -26.1 to -20.6‰ , whereas those of PM_{10} showed a narrow range of -24.4 to -22.4‰ . TC showed positive correlations with $\delta^{13}C$ and with LG (and $nss-K^+$) during the campaign, suggesting an influence of biomass burning including domestic wood burning and field burning of agricultural wastes. $\delta^{13}C$ of TC showed that average contributions of C_4 plants were 41% in both $PM_{2.5}$ and PM_{10} . During dry season, $\delta^{13}C$ of fine particles are more enriched with ^{13}C than coarse particles, suggesting more contribution from burning of C_4 plants under the dry conditions. $\delta^{15}N$ ranged from 13.4 – 22.1‰ (mean: $+16.2 \pm 2.7\text{‰}$) in $PM_{2.5}$ and 10.4 – 18.7‰ (mean: $+13.7 \pm 2.3\text{‰}$) in PM_{10} . $\delta^{15}N$ showed higher ratios in fine particles than coarse particles in both wet and dry season. The larger $\delta^{15}N$ in fine fraction suggests an isotopic enrichment of ^{15}N in the particles during gas (NH_3) and particle $[(NH_4)_2SO_4]$ partitioning

reaction. We also found that NH_4^+ accounts for up to 88.7% of TN in fine aerosols.

5. Acknowledgement

This study was in part supported by the Japan Society for the Promotion of Science (JSPS) through grant-in-aid No. 24221001 and the Environment Research and Technology Development Fund (B-0903) from the Ministry of the Environment, Japan. S.M. acknowledges the financial support by JSPS. We thank Mr. Filbert T. Sogomba of the Department of Physical Sciences (SUA) for sample collection and Chandra M. Pavuluri for his valuable comments. 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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