

Physicochemical and Microbiological Variations in Rivers on the Foothills of Mount Meru, Tanzania.

A. J. Kitalika, R. L. Machunda, H. C. Komakech, K. N. Njau

Abstract- Little is known on the physicochemical and microbiological changes in Nduruma, Tengeru and Maji ya Chai Rivers. Such important variations were studied during wet and dry seasons in 2015. Water samples from various predetermined points of the rivers were analyzed for major physicochemical and microbial contents using APHA standard methods. Pollution levels in Tengeru River were lower than those of Nduruma and Maji ya Chai Rivers. The fecal coliforms were found in all water samples whereas other parameters were found to be within the WHO maximum permissible limits in most samples. Few samples had BOD, nitrates and total soluble phosphates levels higher than the WHO of 10 mg/l, 50 mg/l and 0.1 mg/l, respectively. Most areas in wet season recorded COD levels higher than the WHO recommended values of 10 mg/l. Few areas in the dry season had EC of up to 1722 $\mu\text{S}/\text{cm}$ which is above the WHO maximum recommended level of 500-1500 $\mu\text{S}/\text{cm}$. The stable isotopes studies in water samples revealed sources of DOC in Nduruma River was from plant materials and soil composite with its nitrates being mainly from urea fertilizers applied by farmers. Ground water was the main source of DOC in headwater of Tengeru while manure was its main source in the floodplain with its nitrates originating from animal manure. DOC in Maji ya Chai River originated from plant materials whereas the nitrates was from wild animal manure. The observed severe degradations of the riparian environment of the rivers call upon immediate rehabilitation measures.

Index Terms- physicochemical changes, microbiological properties, Nduruma River, Tengeru River, Maji ya Chai River, stable isotopes, pollutant sources.

1 INTRODUCTION

Tanzania is among the countries with abundant fresh water sources which conservation outside of large towns is lacking or minimal at best [1]. Among these sources include rivers and lakes. It is known that over 1.6 billion people lack access to clean water with more than 2.6 billion do not have proper sanitation the situation being most dominant in developing countries including Tanzania [2]. Temi, Nduruma, Tengeru and Maji ya Chai Rivers are among the fresh water sources in the Pangani basin supplying the Arusha and Meru Urban in Tanzania[3].

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The mentioned rivers pass through the human settlements and downstream to the areas with several human activities which include farming, building material mining and pastoralism. Such different environmental changes cause changes in the water chemistry which result into polluted water as they move. Water pollution which leads to physicochemical changes and other parameters does not only threaten the human health but also increase the cost of water processing for domestic and other purposes of use. Such water pollution include the change in physical, chemical and biological properties of water which prevent its suitability for various purposes [4]. The changes in water quality in these rivers is advocated to be caused by poor Waste Stabilization Ponds (WSP) effluent quality, which does not meet the Tanzania effluent quality standard for receiving rivers [5], poor agricultural practices, urban planning, poor hygienic conditions of human settlements and mining activities.

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Despite the established cause for water deterioration in these rivers, the pollutants and extent of such pollution in different aspects is unknown. Considering the importance of these rivers, a study was designed to unveil and assess such unknown pollutants through different scientific methods. Therefore, this paper reports the changes in physicochemical and biological properties of water in the three rivers namely, Nduruma, Tengeru and Maji ya Chai and how the rivers are affected by seasonal changes and surrounding environment.

2 MATERIALS AND METHODS

2.1 Description of Study Area

The study area involved Nduruma, Tengeru and Maji ya Chai Rivers. These rivers originate from common sub catchments of Pangani basin in the foot hills of Mount Meru lying from the eastern part to the south west of the mountain (Fig. 1). The rivers run downstream from the mountain to the south east draining their contents in Kikuletwa river [6]. The natural vegetation is typically tropical forest to savannah. The topography of the study region is dominated by the Mount Meru volcanic cone of Pleistocene to recent origin. The local climate of the area is temperate Afro-Alpine, with an annual precipitation of 450 mm [7] and means minimum and maximum daily temperature of 20.6°C and 28.5°C, respectively. The rainfall is irregularly distributed between a main wet season from February to mid May (contributing 70% of the annual precipitation), and a minor one from September to November which provides much of the remainder giving the mean annual rainfall of 535.3 mm [8], [9]. The study area was divided into three regions depending on the river and land development namely pristine (headwater) (3° 15' 00" S to 3° 20' 00" S), middle/urban (3° 20' 00" S to 3° 25' 00" S) and floodplain (3° 25' 00" S to 3° 35' 00" S). The catchment area for the rivers (headwater) is characterized by both artificial and natural forest conservation; middle area of the river consists of mixed agriculture and urban settlement. The floodplain (downstream) region is characterized by bare land, intensive grazing, large scale agriculture and serious flooding in wet season.

2.2 Sampling

The GPS predetermined sampling points were identified basing on confluence, accessibility and pre established monitoring stations. In each sampling point two litres of water samples were collected of which one litre was used for chemical parameter measurements and the second litre for microbiological and nutrients measurement. Sampling was done thrice in one week interval during the wet season (Mid-March to early April) and dry season (August) in 2015. In each season 126 representative samples were collected for analysis.

2.3 Extraction, Pretreatment and Cleanup of Water Samples

Samples for NO_3^- analysis were acidified with conc. H_2SO_4 to a pH below 2 and frozen until respective analysis. Samples for other parameters measurements were not pretreated with any chemical except the samples with solids and other organic debris were filtered using a 0.45 μm filter before measurement. Samples for stable isotope analysis of $\delta^{13}\text{C}$, $\delta^{15}\text{N}$ were preserved with few drops ZnCl_2 (aq) to prevent all biological activities, whereas samples for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ analysis were cooled at 4°C ready for transport at Stable Isotope laboratory to Waterloo University in Canada.

2.4 Analysis and Confirmation

Temperature, pH, total dissolved solids (TDS), dissolved oxygen (DO) and electrical conductivity (EC) were measured in situ using a HANNA multiparameter Model HI9829 whereas the total hardness were measured by acid titrimetric method. Other parameters such as BOD, nitrates (NO_3^-), fecal coliforms and total suspended solids (TSS) were measured following standard methods [10]. In addition, total phosphates (TP) and soluble phosphates (SP), sulphates and chlorides were measured using HACH 2800™ while turbidity and alkalinity were measured using a 2100Q01 HACH portable turbidimeter with formazin turbidity standard 4000 NTU in serial dilutions to the required standards and HANNA alkalinity checker HI 755, respectively. The chromophoric dissolved organic matter (CDOM) was measured in situ by a submersible fluorometer Turner™ Cyclops-7 (PIN-2100-000-U) integrated with a data logger.

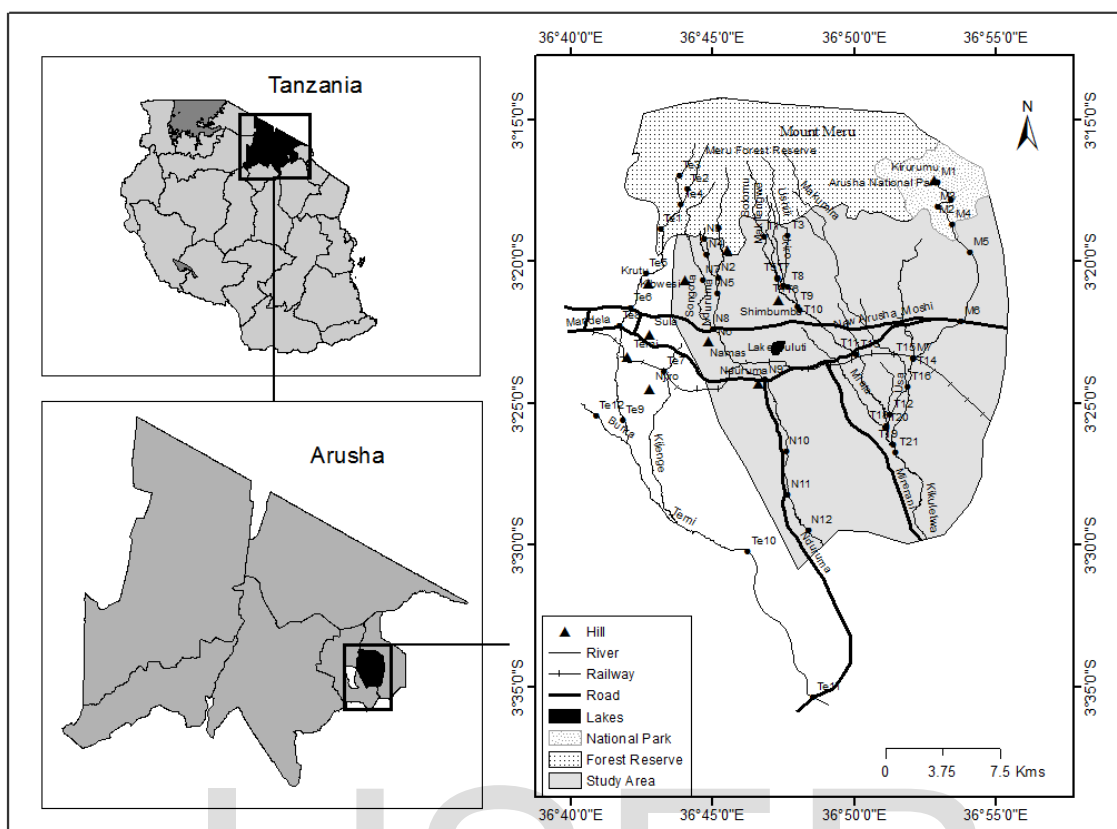


Fig. 1. Location of the Study Area

Analysis for $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ stable isotopes was done using a modern technology of Los Gatos Research Laser processes analyzer with Integrated Cavity Output Spectroscopy (LGR-ICOSTM) machine.

3 RESULTS AND DISCUSSION

The average physicochemical and microbiological trends for the four rivers are shown in **Table 1** through **3**. Also the signatures of the four stable isotopes elements for C, N, H and O are shown in **Table 4**.

3.1 Physicochemical and Microbiological Changes in Nduruma River

The distribution of ions in Nduruma River is shown in **Table 1** and summarized in **Fig. 2**. The major ions pattern in this river showed high levels of chloride (Cl^-) ions than carbonates. The highest levels of ions were observed in dry season than wet season. Highest chloride levels (44.99mg/l) were observed in wet season in the pristine environment (N5) whereas in the dry season the levels were elevated up

to 122.5 mg/l in similar environment at N7. Both amounts were monitored at Songota River which is among the tributaries feeding Nduruma River.

Therefore, under such trend, we can justify that Songota contributed higher Cl^- levels to the downstream although other sources can contribute to some small extents. Despite the high levels observed in dry season, still they are within the maximum permissible threshold levels for Australia of 250 mg/l [11].

Table 1. Water Quality Parameters for Nduruma River

Wet Season														
	FC (FCU/100 ml)	Salinity	pH	T (°C)	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	CO ₃ ²⁻	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	TDS	EC (µS/cm)
Min.	900	0.25	7.63	12.21	2.00	1.21	0.70	0.22	6.57	6.25	15.00	bdl	71.00	142.00
Max.	11000	1.39	9.04	20.48	10.00	10.86	3.78	1.11	43.57	31.26	44.99	9.10	108.00	217.00
Av.	4692	0.66	7.98	17.20	4.57	5.40	1.74	0.54	21.25	15.35	28.82	1.28	90.67	179.33
	TH	NH ₃	NH ₃ -N	NH ₄ ⁺	NO ₃ ⁻	NO ₃ -N	TSP	TP	COD	BOD	CDOM (RFU)	DO	TSS	Turbidity (NTU)
Min.	3.22	0.02	0.01	0.01	4.90	1.10	0.12	2.48	21.00	9.00	-172.00	4.90	bdl	bdl
Max.	19.72	1.84	1.48	1.90	60.00	19.10	0.77	17.27	39.00	23.00	-129.00	10.58	4.92	3.73
Av.	9.96	0.37	0.29	0.36	26.73	4.20	0.41	9.35	30.50	15.72	-155.14	7.04	2.43	1.59
Dry Season														
	FC (FCU/100 ml)	Salinity	pH	T (°C)	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	CO ₃ ²⁻	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	TDS	EC (µS/cm)
Min.	500	bdl	7.40	12.01	1.21	5.00	0.48	0.14	26.92	3.81	45.00	1.35	81.00	88.00
Max.	4000	14.00	9.90	24.32	9.22	38.00	3.61	1.06	92.20	28.92	122.50	23.49	154.00	308.00
Av.	1546	3.50	8.22	19.00	4.63	20.00	1.95	0.58	59.00	15.28	73.12	3.96	117.83	223.42
	TH	NH ₃	NH ₃ -N	NH ₄ ⁺	NO ₃ ⁻	NO ₃ -N	TSP	TP	COD	BOD	CDOM (RFU)	DO	TSS	Turbidity
Min.	6.21	bdl	0.02	0.01	0.01	6.03	0.02	0.16	bdl	7.00	3.00	6.16	bdl	bdl
Max.	47.22	5.16	2.26	1.82	2.34	73.80	0.92	1.06	6.00	31.00	18.10	8.22	1.22	1.80
Av.	24.63	1.44	0.46	0.35	0.44	32.88	0.44	0.57	2.71	18.86	10.35	7.42	0.45	0.52

Note: All unitless values are in mg/l except pH. **Min.** - Minimum, **Max**- Maximum, **Av.** - Average

Table 2. Water Quality Parameters for Tengeru River

Wet Season														
	FC (FCU/100 ml)	Salinity	pH	T (°C)	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	CO ₃ ²⁻	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	TDS	EC (µS/cm)
Min.	1300	0.08	7.12	15.00	0.48	1.21	0.62	0.33	10.14	7.27	2.50	bdl	37.00	72.00
Max.	11500	1.18	7.58	18.81	8.20	12.18	3.62	1.94	42.46	39.13	24.99	10.00	260.00	518.00
Av.	4174	0.39	7.34	17.53	2.35	3.76	1.48	0.80	17.74	16.29	13.79	1.20	110.81	221.52
	TH	NH ₃	NH ₃ -N	NH ₄ ⁺	NO ₃ ⁻	NO ₃ -N	TSP	TP	COD	BOD	CDOM (RFU)	DO	TSS	Turbidity (NTU)
Min.	3.21	0.01	0.01	0.01	0.80	0.10	0.07	1.40	2.60	bdl	-181.00	6.45	bdl	bdl
Max.	16.68	1.10	0.99	1.30	18.40	4.13	0.29	5.80	97.00	44.90	128.00	9.37	31.00	33.90
Av.	7.97	0.31	0.27	0.34	6.44	1.51	0.17	3.43	33.88	15.83	-50.23	8.61	8.70	10.26
Dry Season														

	FC (FCU/100 ml)	Salinity	pH	T (°C)	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	CO ₃ ²⁻	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	TDS	EC (µS/cm)
Min.	9	0.12	7.23	14.00	8.00	1.21	2.56	0.79	19.14	20.15	12.50	bdl	42.00	83.00
Max.	6200	2.41	8.59	21.00	24.00	15.78	8.27	2.56	73.22	62.44	137.00	25.00	243.00	474.00
Av.	1601	0.70	7.90	18.04	12.95	5.88	4.25	1.32	39.99	33.95	42.71	7.89	131.43	262.33
	TH	NH ₃	NH ₃ -N	NH ₄ ⁺	NO ₃ ⁻	NO ₃ -N	TSP	TP	COD	BOD	CDOM (RFU)	DO	TSS	Turbidity (NTU)
Min.	10.04	0.01	0.01	0.01	0.98	0.12	0.12	2.45	2.00	0.20	-178.00	6.66	bdl	bdl
Max.	29.71	1.35	1.22	1.60	22.63	5.08	0.48	9.79	56.00	31.00	-78.50	8.38	24.17	16.92
Av.	18.83	0.38	0.33	0.42	7.92	1.86	0.28	5.79	16.39	9.45	-141.41	7.56	3.31	3.26

Note: All unitless values are in mg/l except pH. **Min.** - Minimum, **Max.**-Maximum, **Av.** Average

Table 3. Water Quality Parameters for Maji ya Chai River

Wet Season														
	FC (FCU/100ml)	Salinity	pH	T (°C)	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	CO ₃ ²⁻	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	TDS	EC (µS/cm)
Min.	4300	0.55	7.37	17.00	0.49	1.21	1.52	0.22	6.57	6.27	bdl	5.00	395.00	791.00
Max.	6900	2.71	8.60	19.48	2.43	6.08	4.56	0.67	32.86	18.82	16.00	39.99	594.00	1187.00
Av.	5544	1.14	8.03	18.27	1.50	3.75	2.95	0.43	20.46	12.21	7.63	18.56	477.14	954.86
	TH	NH ₃	NH ₃ -N	NH ₄ ⁺	NO ₃ ⁻	NO ₃ -N	TSP	TP	COD	BOD	CDOM (RFU)	DO	TSS	Turbidity (NTU)
Min.	bdl	0.02	0.01	0.02	1.60	0.30	0.05	1.31	4.00	2.00	-98.60	0.54	bdl	82.60
Max.	2.01	0.81	0.76	0.93	16.50	4.10	0.51	11.60	74.00	41.00	326.60	8.87	2.01	361.60
Av.	0.53	0.35	0.31	0.40	8.18	1.96	0.35	7.78	26.89	14.44	136.53	5.53	0.72	160.42
Dry season														
	FC (FCU/100ml)	Salinity	pH	T °C	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	CO ₃ ²⁻	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	TDS	EC (µS/cm)
Min.	300	0.41	7.91	17.37	10.00	2.43	3.77	1.10	3.35	31.14	35.00	11.00	448.00	896.00
Max.	6900	6.12	9.60	21.44	14.00	7.28	5.28	1.53	4.69	43.59	87.50	30.00	861.00	1722.00
Av.	3611	2.21	8.57	19.95	11.25	3.81	4.33	1.26	3.85	35.81	58.23	23.98	591.86	1183.43
	TH	NH ₃	NH ₃ -N	NH ₄ ⁺	NO ₃ ⁻	NO ₃ -N	TSP	TP	COD	BOD	CDOM (RFU)	DO	TSS	Turbidity (NTU)
Min.	13.23	0.03	0.01	0.03	2.24	0.42	0.08	0.15	5.00	3.00	-97.40	0.10	bdl	bdl
Max.	17.64	1.13	1.06	1.30	23.10	5.74	0.81	19.66	149.00	77.00	180.70	7.97	3.02	4.61
Av.	15.07	0.49	0.44	0.55	11.45	2.74	0.56	12.53	46.11	24.56	56.23	5.81	1.42	1.72

Note: All unitless values are in mg/l except pH. **Min.** - Minimum, **Max.**-Maximum, **Av.** Average, bdl-below detection limit

Table 4. Stable Isotopic Signatures and Dissolved Organic Carbon Levels for Nduruma, Tengeru and Maji ya Chai Rivers.

Sampling Point	Nduruma River			Tengeru River			Maji ya Chai River			Manure			Soil Composite			GW			Fertilizers		Plant Materials		
	N1	N6	N12	T3	T9	T19	M1	M5	M7	N	T	M	N	T	M	N	T	M	UREA	DAP	N	T	M
DOC (mg/l)	bdl	0.2	0.2	0.74	0.99	1.3	2.31	2.26	1.96	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{13}\text{C} \pm 0.2$ (‰)	-	-20.36	-22.42	-15.30	-15.47	-13.39	-22.81	-22.23	-22.08	-20.11	-17.11	-22.1	-20.87	-17.94	-19.47	-17.91	-15.13	-15.33	-	-	-21.07	-21.31	-22.1
$\delta^{15}\text{N-NO}_3^- \pm 0.3$ (‰)	+3.72	+7.91	+8.07	+8.16	+9.33	+9.84	+10.46	+10.04	+10.37	+8.29	+8.06	+10.12	+10.61	+9.02	+10.16	+13.06	+3.11	+12.96	+7.95	+6.64	+10.46	+10.13	+9.79
$\delta^{18}\text{O-NO}_3^- \pm 0.8$ (‰)	+0.94	+1.70	+1.92	+1.97	+7.73	+7.91	+8.64	+8.01	+8.02	+1.94	+1.90	+8.11	+8.50	+7.69	+8.12	+9.02	+0.93	+8.99	+1.72	+1.57	+8.12	+8.12	+7.87
$\delta^2\text{H} \pm 0.8$ (‰)	-28.54	-24.83	-18.04	-21.95	-20.85	-19.70	-21.68	-19.11	-14.85	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$\delta^{18}\text{O} \pm 0.2$ (‰)	-5.80	-5.22	-3.99	-4.84	-4.57	-4.40	-4.68	-4.20	-3.28	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Note: N-Nduruma, T-Temi, M-Maji ya Chai. DAP-Double Ammonium Phosphate, GW- Ground Water

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Sulfates (SO_4^{2-}) is another ion of interest in the river whereby the maximum level of 9.10 mg/l was detected at the floodplain (N12) and 23.49 mg/l was recorded at the pristine environment (N3) during wet and dry season, respectively. Low levels in wet season may be caused by dilution from runoff of which in the dry season is absent. Other ions which are HCO_3^- , CO_3^{2-} , K^+ , Na^+ , Mg^{2+} and Ca^{2+} were all in low amount in both seasons and complied to the WHO prescribed standards, despite the high levels in dry season compared to wet season. The WHO requires K^+ levels of 300 mg/l/day and Na^+ at aesthetic level of 180 mg/l where as Mg^{2+} and Ca^{2+} are prescribed in total hardness standards [11]–[13].

3.2 Physicochemical and Microbiological Changes in Nduruma River

The distribution of ions in Nduruma River is shown in **Table 1** and summarized in **Fig. 2**. The major ions pattern in this river showed high levels of chloride (Cl^-) ions than carbonates. **Fig. 2 a, b** summarizes the physicochemical changes in the river. The highest levels of ions were observed in dry season than wet season. Highest chloride levels (44.99 mg/l) were observed in wet season in the pristine environment (N5) whereas in the dry season the levels were elevated up to 122.50 mg/l in similar environment at N7. Both amounts were monitored at Songota River which is among the tributaries feeding Nduruma River. Therefore, under such trend, we can justify that Songota contributed higher Cl^- levels to the downstream although other sources can contribute to some small extents. Despite the high levels observed in dry season, still they are within the maximum permissible threshold levels for Australia of 250 mg/l [11]. Sulfates (SO_4^{2-}) is another ion of interest in the river whereby the maximum level of 9.10 mg/l was detected at the floodplain (N12) and 23.49 mg/l was recorded at the pristine environment (N3) during wet and dry season, respectively. Low levels in wet season may be caused by dilution from runoff of which in the dry season is absent. Other ions which are HCO_3^- , CO_3^{2-} , K^+ , Na^+ , Mg^{2+} and Ca^{2+} were all in low amount in both seasons and complied to the WHO prescribed standards, despite the high levels in dry season compared to wet season. The WHO requires K^+ levels of 300 mg/l/day and Na^+ at aesthetic level of 180 mg/l where as Mg^{2+} and Ca^{2+} are prescribed in total hardness standards [11]–[13].

The status of oxygen demanding wastes were relatively higher in the wet season than dry season (**Fig. 2 c, d**). The maximum levels of COD and BOD in the wet season were 39.00 mg/l and 23.00 mg/l, respectively whereas in the dry season they were 6.00 mg/l and 31.00 mg/l, respectively. Low values for these pollutants in the dry season are a result of runoff absence thus no inputs for oxygen demanding waste from outside the river. Many BOD values in both seasons were higher than WHO prescribed values of 10 mg/l in most sampling points with these values being within the recommended limits in the dry season at N1, N11 and N12 in wet and N3 and N7 in dry season [13]. The DO trends went inversely proportional to COD and BOD with the highest DO being 10.58 mg/l and 8.22 mg/l in wet and dry season, respectively. Similar trends of TSS were measured in respective sampling points. The CDOM being the good indicator of amounts of dissolved carbons, highest levels were registered in sampling points with low COD and BOD an indication that at low oxygen, most organic carbons are being converted into fulvic and humic acids. The highest level of 18.10 RFU was registered at N12 in the dry season. Such low RFU levels indicate low levels of dissolved organic carbons.

Nitrates and phosphates nutrients were also measured in both seasons. High nitrates were measured in the dry season than wet season. The high levels of nitrates were recorded in water in sampling points with high levels of DO such as N5, N9 and N12. The Denitrification was slightly favoured at N3 which was recorded at low pH of 7.4. At acidic pH, transformation of nitrate into reduced states is much favored [14] but in this study there is no elevated levels of NH_3 and NH_4^+ since the water pH could not favour such high transformation due to high pH(alkaline environment). The maximum levels of NO_3^- was 60 mg/l in the wet season and in the dry season the levels were elevated to 73.8 mg/l both being higher than the WHO maximum recommended levels of 50 mg/l [15]. The levels of TP were significantly higher in wet season with the highest level of 17.27 mg/l at Songota stream (N8) while the dry season recorded very low levels.

In wet season the TSP were above the recommended levels for the river while most parts of the river recorded levels below the maximum recommended level of 0.1 mg/l (**Fig. 3 a, b**).

Fig. 3 c, d also describes the distribution of fecal coliforms with respect to other physicochemical parameters. The wet season recorded higher amount of fecal coliforms than dry season. Higher amount were recorded in the flood plain than in the other parts of the river during wet season. The middle part of the river experienced high amount in the dry season whereas its floodplain the amount decreased significantly. Higher amount of FC in the wet seasons is caused by runoff which carried contaminated wastes to the river. The headwater of the river (N1 and N2) recorded low amounts of FC in both seasons. The highest amount of FC was 11000 FCU/100 ml in the wet season which was recorded at N12 and its highest amount of 4000 FCU/100 ml was recorded at N3 in the dry season. Higher salinity content was recorded in the dry season than wet season probably the later being affected by dilutions from runoff. The highest level in the dry season was 1.19 mg/l while in the dry season an elevated level of up to 13.90 mg/l both values being recorded at N5. The maximum recorded levels were lower than the maximum permissible levels of 100 mg/l [11]. Acceptable range of pH were recorded in all areas of the river except at one point (N6) in the dry season which had pH 9.90 which is above the maximum WHO recommended level of 8.5 [15]. The levels of TH, EC and TDS were within the recommended limits as per WHO standards.

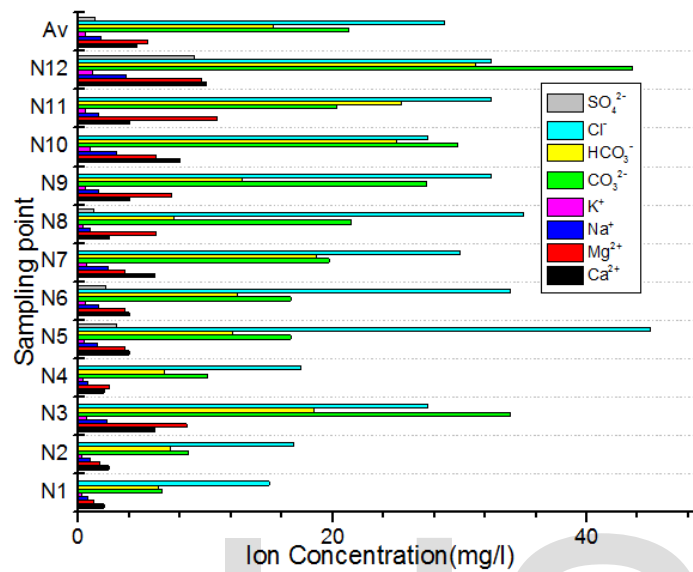
3.3 Physicochemical and Microbiological Changes in Tengeru River

Fig. 4 a, b summarizes the general trends of major ions in Tengeru River. The wet season was dominated by HCO_3^- and CO_3^{2-} while the other ions remained moderately low. The highest recorded value for HCO_3^- and CO_3^{2-} was 39.13 mg/l at T20 and 42.46 mg/l at T16, both being in the floodplain. The dry season recorded higher levels of other ions in addition to SO_4^{2-} . The highest levels of HCO_3^- , CO_3^{2-} and SO_4^{2-} were 62.44 mg/l at T10 and 73.22 mg/l at T14 and 137.00 mg/l at T8, respectively. The maximum Cl levels were within the maximum threshold levels for Australia of 250mg/l [11].

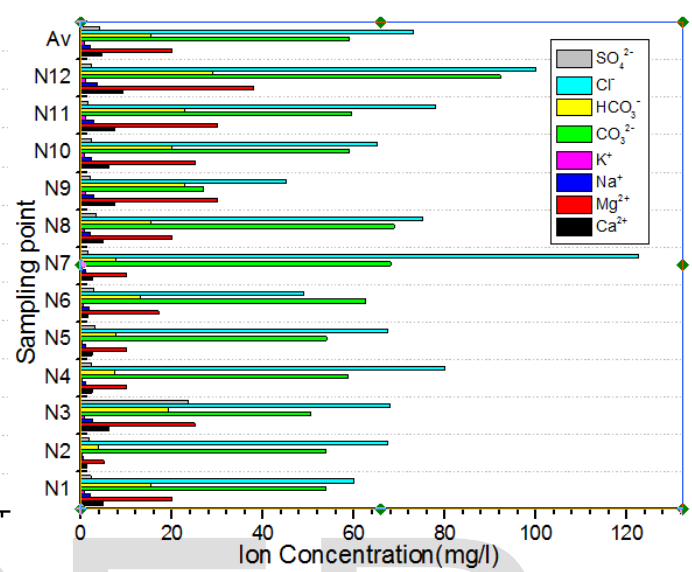
Distribution of oxygen demanding wastes, carbon chromophores and other solids are presented in **Fig. 4 c, d**. The BOD was unevenly distributed in the river. Highest levels of 44.90 mg/l and 31.00 mg/l were recorded at T18 in both wet and dry season, respectively. These levels

increased proportionally with increase in COD where the highest levels of 97.00 mg/l and 56.00 mg/l were recorded in the same point. Most water of the middle and floodplain exceeded the maximum WHO recommended limits [15]. DO trends were inversely proportional to the COD and BOD levels. The high levels between 9.28 mg/l and 9.37 mg/l was recorded in the headwater and in the floodplain it ranged between 9.17 mg/l and 9.29 mg/l all in the wet season whereas a slightly fall in the dry season were recorded at T5 (8.38 mg/l), T19 (8.25 mg/l) and T20 (8.24 mg/l). The rest part of the river had a DO range between 6.45 mg/l and 7.85 mg/l. Usually streams with high dissolved oxygen concentrations >8 mg/L are considered healthy streams thus in our study, most part of the river was healthy. The chromophoric dissolved organic matters (CDOM) were higher in the floodplain during wet season an indication of high dissolved organic carbons in the floodplain. The negative values in the dry season indicate the dissolved organic matter were below the detection limit of the instrument with the negative deviation range from the minimum detectable level. The general trends for total suspended solids (TSS) increased with increase in CDO and BOD an indication that TSS is part of oxygen demanding wastes. These values were up to 31.00 mg/l and 24.17 mg/l in the wet and dry season, respectively which most of them exceeded the recommended values of 5 mg/l in the floodplain [16, 17]. Turbid water exceeding the maximum permissible levels was noted at T12 (33.90 NTU), T18 (37.39 NTU) and T21 (32.80 NTU) in wet season whereas in dry season it dropped down to T12 (11.98 NTU) and T19 (16.92 NTU) as a result of absence of runoff.

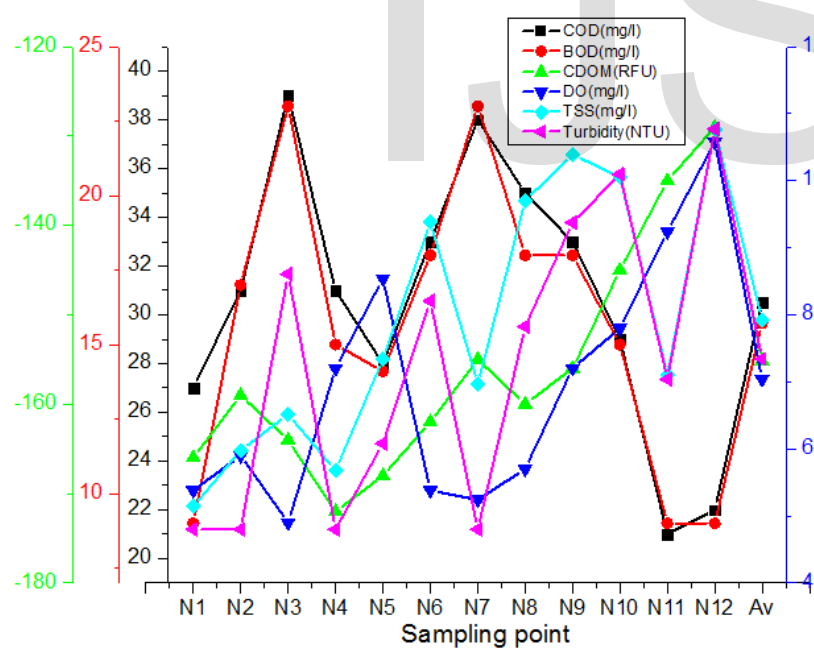
The nitrates (NO_3^-) were recorded in all sampling points in both seasons. Higher levels were recorded in dry than wet season. Nitrates levels in the wet season ranged between 0.8 mg/l to 18.40 mg/l where as in dry season the values were 0.98 mg/l to 22.63 mg/l. Other nitrates intermediates remained very low. The highest levels of NO_3^- (18.40 mg/l wet season, 22.63 mg/l dry season) were detected at T12 in both seasons.



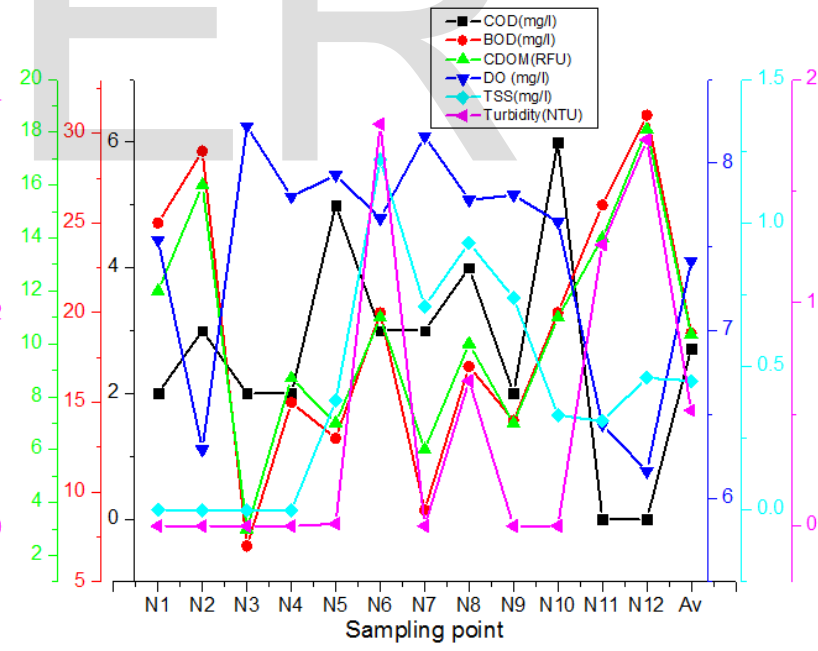
(a)



(b)



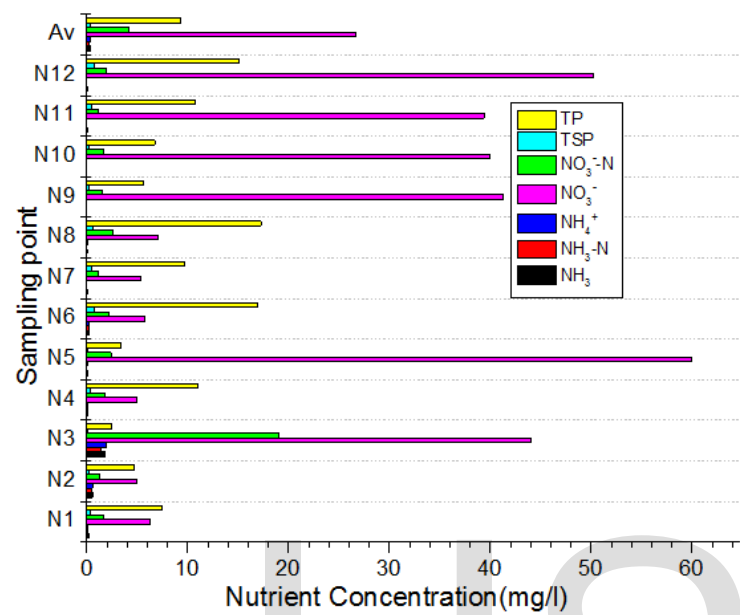
(c)



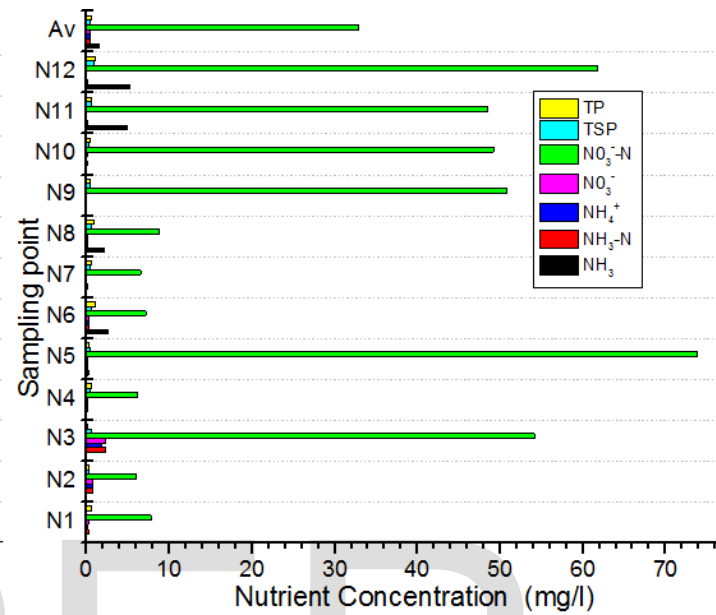
(d)

Fig. 2. Major Ions and Physicochemical Variation in Wet (a, c) and Dry (b, d) Seasons for Nduruma River

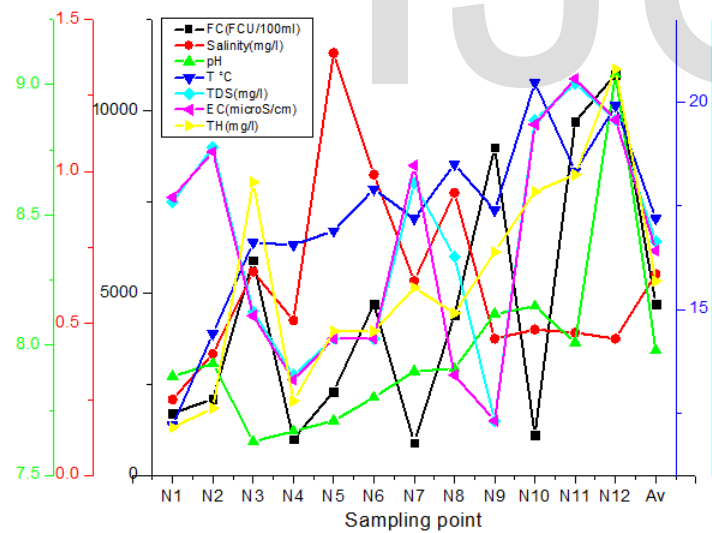
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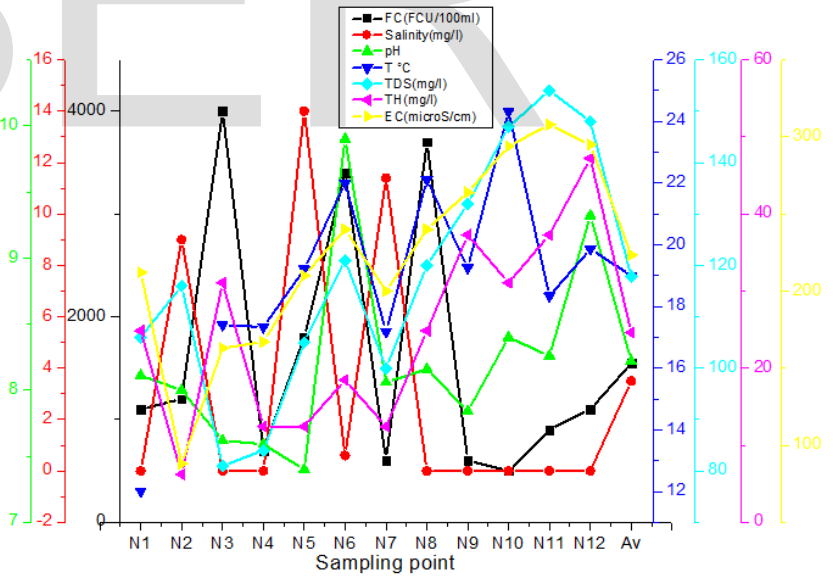
(a)



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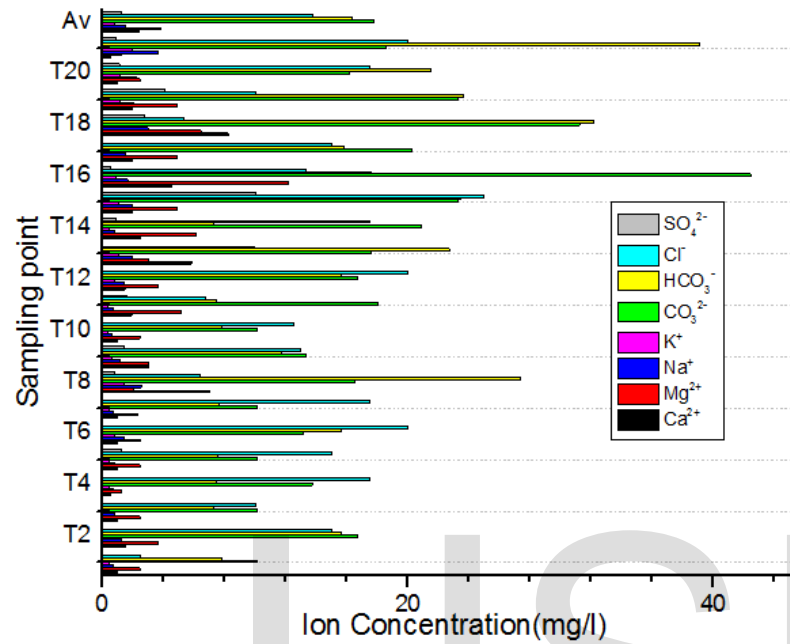
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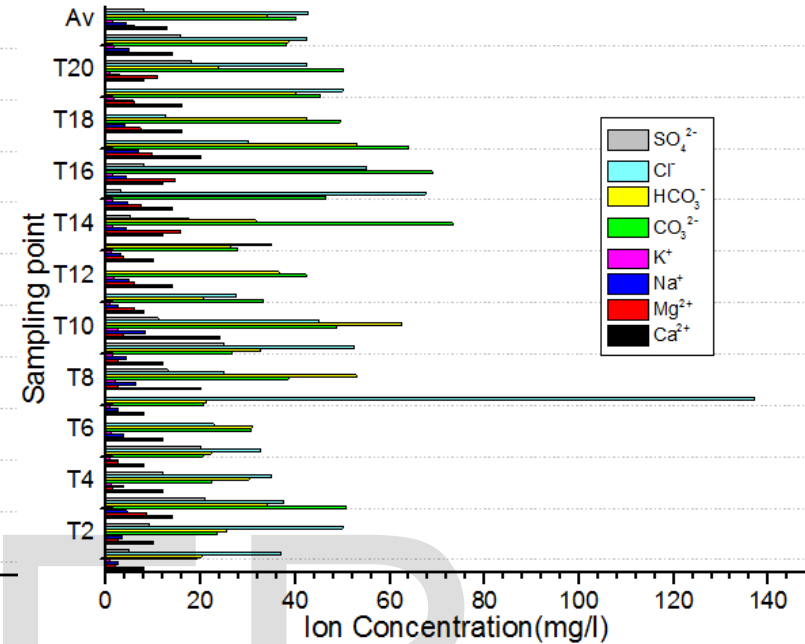
(d)

Fig. 3. Physicochemical and Nutrients Variation in Wet (a, c) and Dry (b, d) Season for Nduruma River

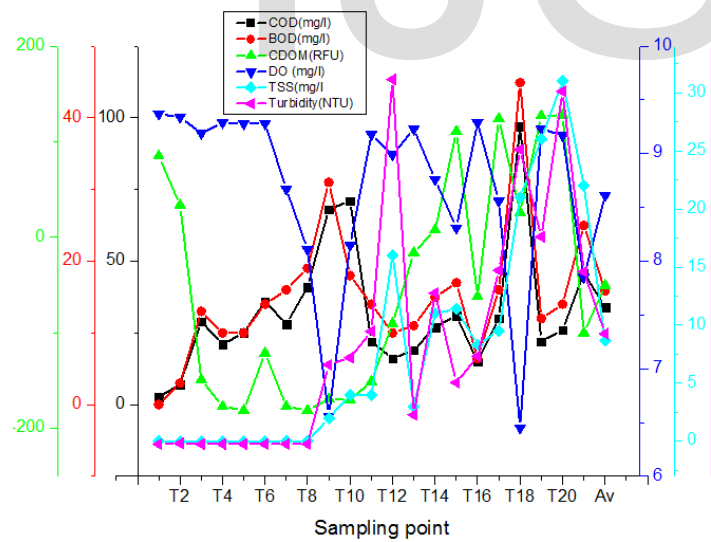
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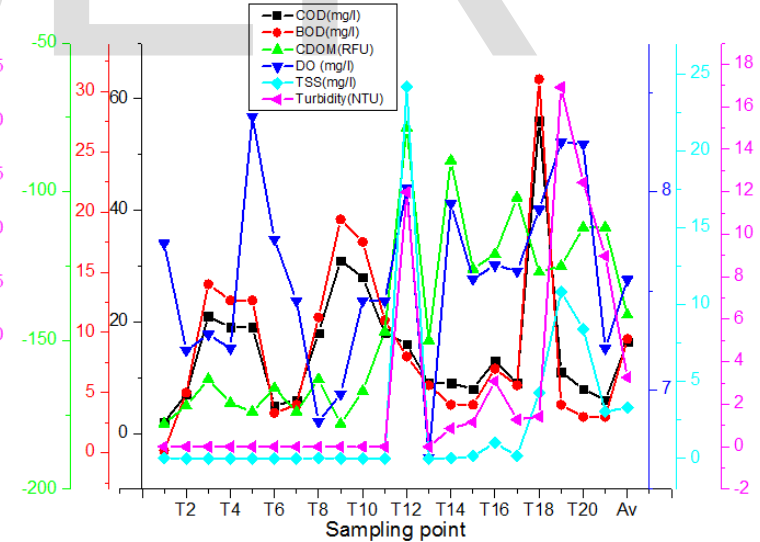
(a)



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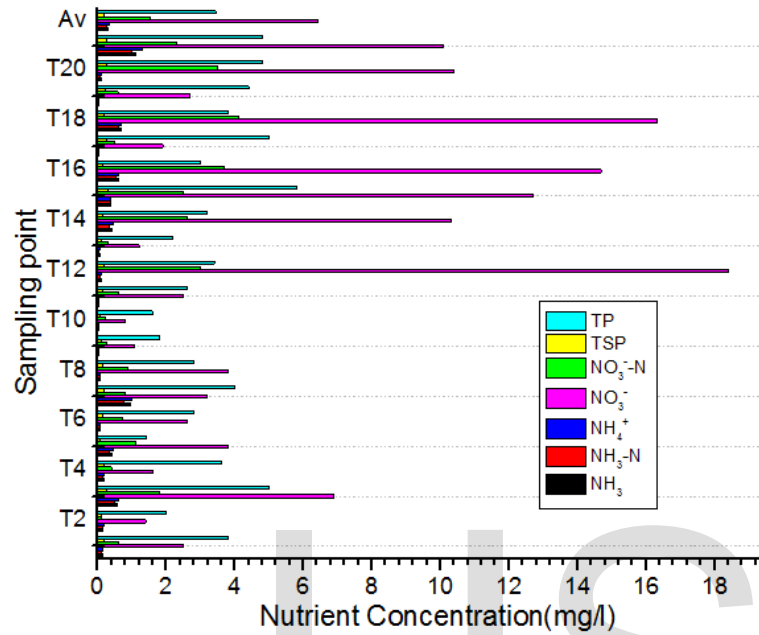
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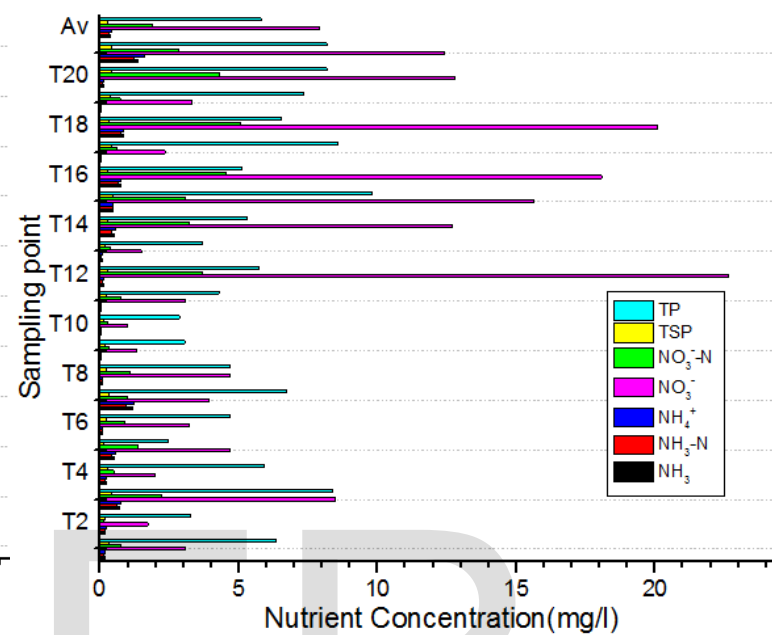
(d)

Fig. 4. Major Ions and Physicochemical Variation in Wet (a, c) and Dry (b, d) Seasons for Tengeru River

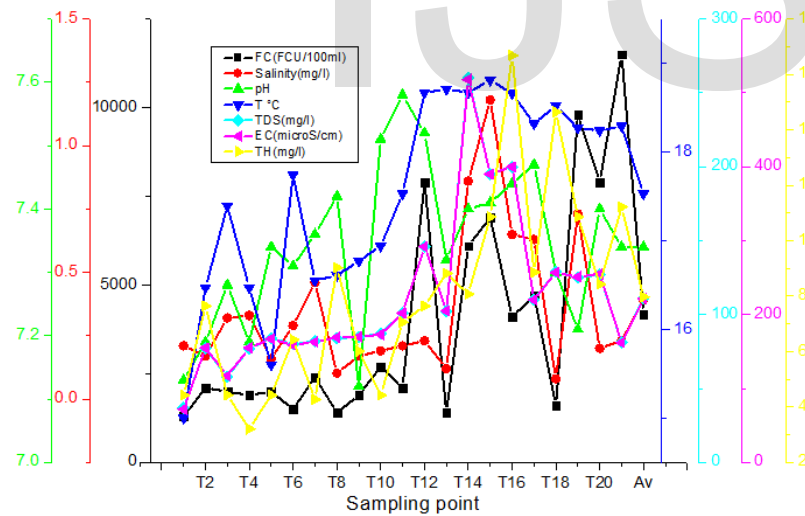
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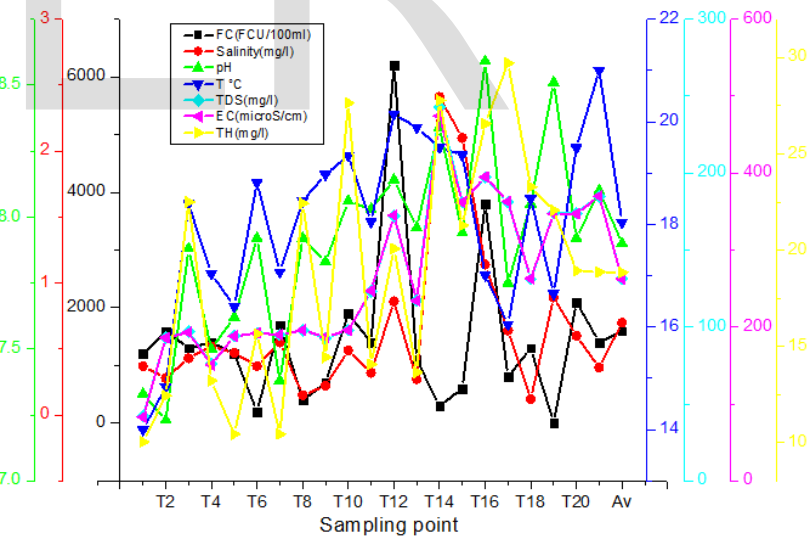
(a)



(b)



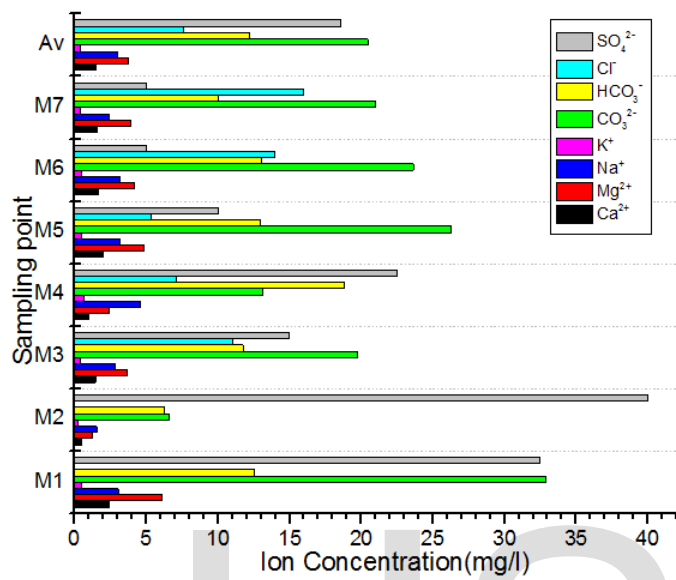
(c)



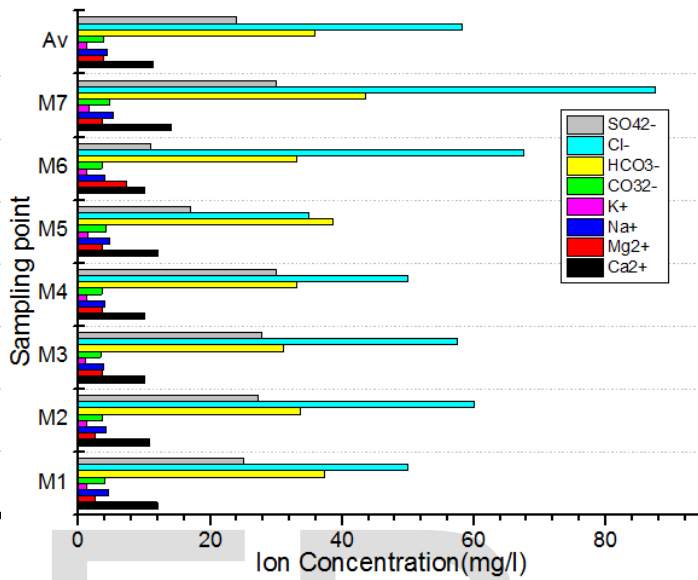
(d)

Fig. 5. Physicochemical and Nutrients Variation in Wet (a, c) and Dry (b, d) Season for Tengeru River

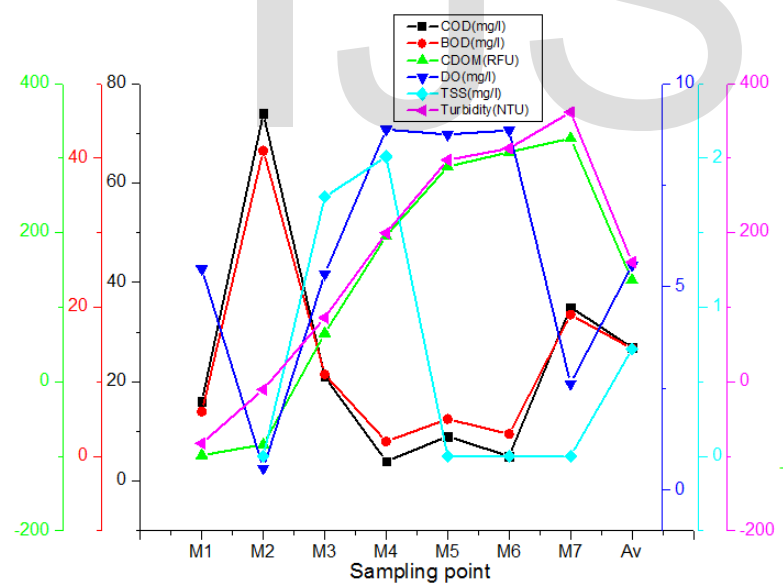
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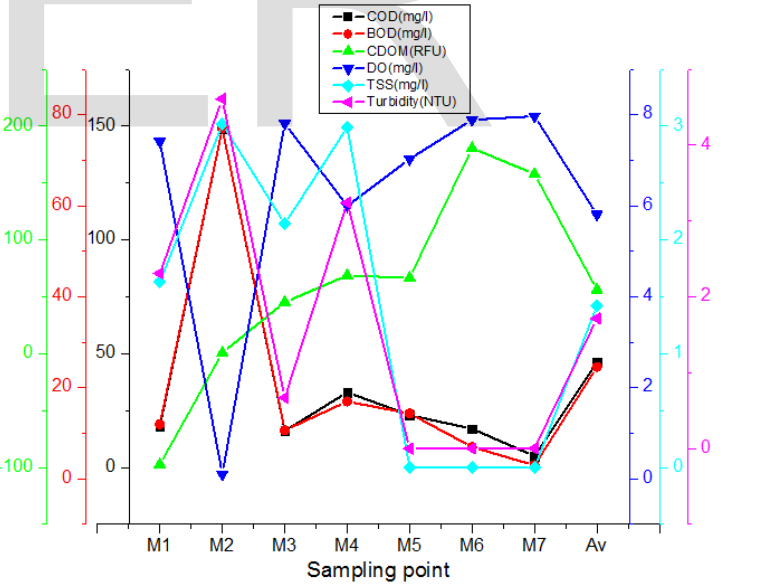
(a)



(b)



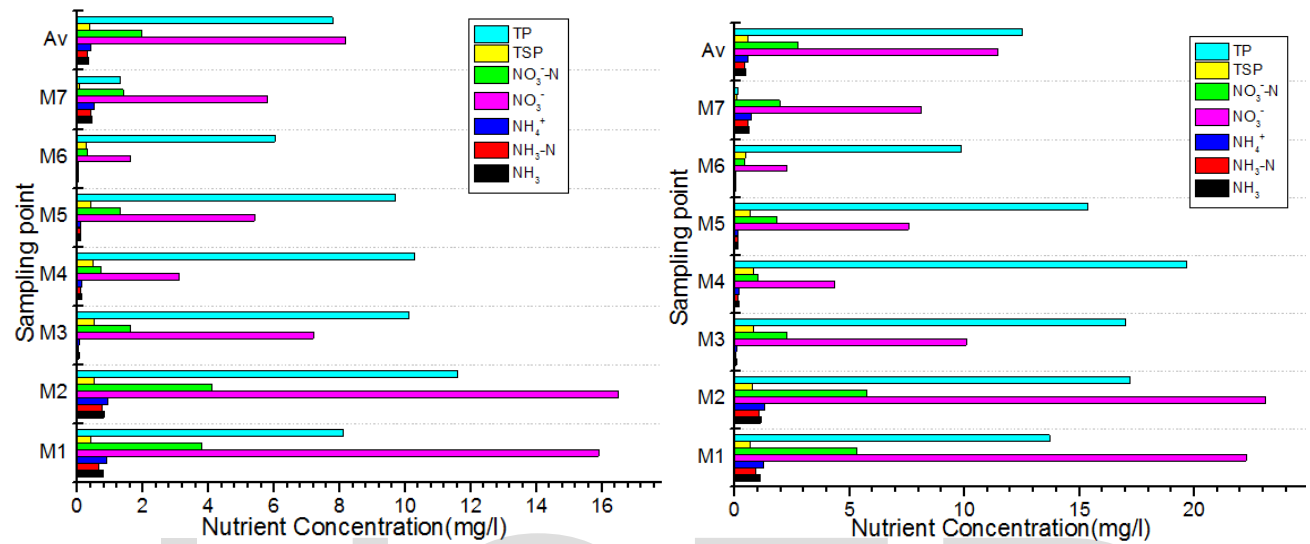
(c)



(d)

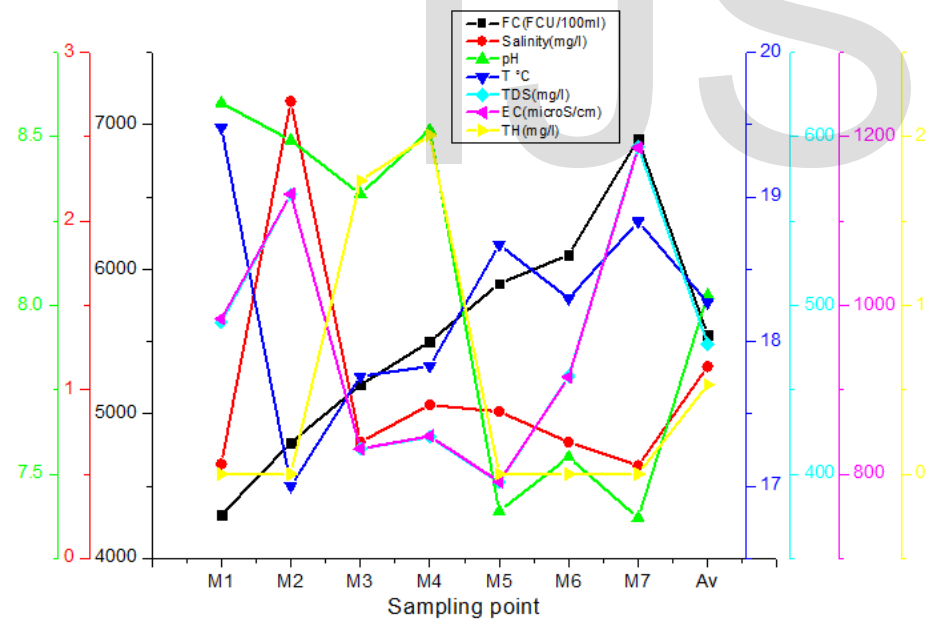
Fig. 6. Major Ions and Physicochemical Variation in Wet (a, c) and Dry (b, d) Seasons for Maji ya Chai River

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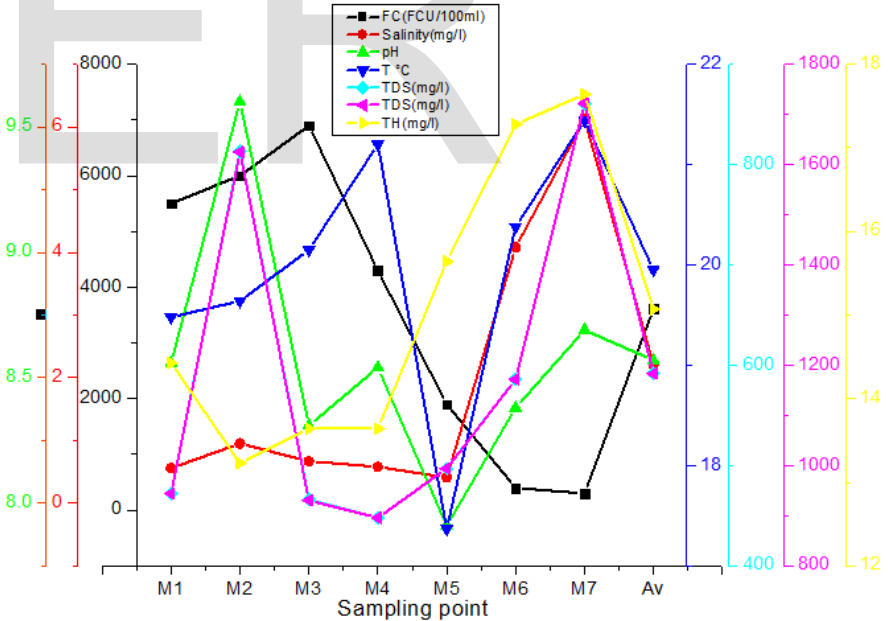


(a)

(b)



(c)



(d)

Fig. 7. Physicochemical and Nutrients Variation in Wet and Dry Season for Maji ya Chai River

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In addition the nitrates levels of this river were lower than those of Nduruma and Maji ya Chai Rivers due to less agricultural practices along the river which could be among of the nitrates sources of the river. All nitrates levels in this river were within the maximum permissible levels of 50 mg/l as stipulated by WHO. However, phosphates nutrients PO_4^{2-} were lower than nitrates in most samples. The amount of readily available phosphates (TSP) ranged between 0.07mg/ to 0.29 mg/l and 0.12 mg/l to 0.48 mg/l in wet and dry seasons, respectively. Higher levels of PO_4^{2-} were recorded in the dry than wet season and their low levels in the wet season may be associated with dilution and adsorption of phosphate molecules in organic matter due to its higher affinity in it. Despite to the overall low levels of readily available phosphates in water, most levels were above the maximum recommended limits of 0.1 mg/l for a river discharging into the lake or ocean [15]. Turbid water exceeding the maximum permissible levels was noted at T12 (33.90 NTU), T18 (37.39 NTU) and T21 (32.80 NTU) in wet season whereas in dry season it dropped down to T12 (11.98 NTU) and T19 (16.92 NTU) as a result of absence of runoff.

The nitrates (NO_3^-) were recorded in all sampling points in both seasons. Higher levels were recorded in dry than wet season. Nitrates levels in the wet season ranged between 0.8 mg/l to 18.40 mg/l where as in dry season the values were 0.98 mg/l to 22.63 mg/l. Other nitrates intermediates remained very low. The highest levels of NO_3^- (18.40 mg/l wet season, 22.63 mg/l dry season) were detected at T12 in both seasons. In addition the nitrates levels of this river were lower than those of Nduruma and Maji ya Chai Rivers due to less agricultural practices along the river which could be among of the nitrates sources of the river. All nitrates levels in this river were within the maximum permissible levels of 50 mg/l as stipulated by WHO (Fig. 5 a, b). However, phosphates nutrients PO_4^{2-} were lower than nitrates in most samples. The amount of readily available phosphates (TSP) ranged between 0.07 mg/ to 0.29 mg/l and 0.12 mg/l to 0.48 mg/l in wet and dry seasons, respectively. Higher levels of PO_4^{2-} were recorded in the dry than wet season and their low levels in the wet season may be associated with dilution and adsorption of phosphate molecules in organic matter due to its higher affinity in it. Despite to the overall low levels of readily available phosphates in water, most levels were above the maximum

recommended limits of 0.1 mg/l for a river discharging into the lake or ocean [15].

The fecal coliforms (FC) in Tengeru River were higher in the wet season than dry season with the headwater environment being lower than the rest parts of the river (Fig. 5 c, d). The minimum number of fecal coliforms was 1300 FCU/100 ml where as its highest was 11,500 FCU/100 ml in the wet season whereas in the dry season the values dropped to a range between 9 FCU and 6200 FCU. Fecal coliforms in the human settlement parts of the river can be associated with poor hygienic practices of the surrounding environment which involve improper use of latrines and sewage waste disposal. Thus, proper treatment of this water for drinking is important in order to kill germs. The floodplain experienced higher amount of FC than the rest parts of the river in the wet season. Very low salinity levels in this river were recorded with the highest level in the wet and dry seasons being 1.18 mg/l and 2.41 mg/l respectively. The pH of water was within the WHO standards and ranged between 7.12 and 8.59 in both seasons. The TDS were within the prescribed standards of 1200 mg/l in both seasons with highest level of 260 mg/l being recorded at T14 in the wet season [15]. Similar trends were demonstrated by EC where the maximum recorded level of 518 $\mu\text{S}/\text{cm}$ was within the required standards. Hardness is another issue of concern whereby the very low levels were recorded with its maximum level being 16.68 mg/l and 29.71 mg/l in wet and dry season thus soft water.

3.3 Physicochemical and Microbiological Changes in Maji ya Chai River

As it is seen in Fig. 6 a, b, the SO_4^{2-} , Cl^- , HCO_3^- and CO_3^{2-} dominated in the wet season. Sulphates recorded the highest concentration (39.99 mg/l) compared to other ions followed by CO_3^{2-} (32.86 mg/l) both being recorded at the headwater of the river (M1 and M2). Other ions remained relatively low in most sampling points. However, the highest concentrations of ions were recorded in the dry season an indication of dilutions for their low levels in the wet season. In this season, higher concentrations were recorded for Cl^- and HCO_3^- in up to 87 mg/l and 43.59 mg/l, respectively where other ions were significantly low. In this season, the floodplain environment recorded the highest levels of ions than the headwater environment. Other ions ranged from 0.22 mg/l to 1.53 mg/l (K^+), 1.52 mg/l to 5.28 mg/l (Na^+), 1.21

mg/l to 7.28 mg/l (Mg^{2+}) and 0.49 mg/l to 14.00 mg/l (Ca^{2+}). All ions concentrations levels were below the maximum recommended limits by WHO [11], [15].

The oxygen demanding wastes were another important parameter studied in the river. The headwater and middle part of this river showed highest oxygen demanding wastes than other rivers specifically during dry season. Higher values of COD and BOD in dry season are a different case experienced in this river where the opposite was expected. This is due to the fact that there is a major common source for the oxygen demanding wastes where high amount of organic matter are released, the foots of Kirurumu hill, such that during wet season there is continuous dilutions lowering their concentration.

The COD and BOD varied proportionally to each other with higher amounts being recorded in pristine environment in both seasons. In the wet season, the highest COD was 74.00 mg/l recorded at M2 and its lowest was 4.00 mg/l recorded at M4. The highest levels in the dry season was 149.00 mg/l where as its lowest was 3.35 mg/l. Most areas in the wet season recorded values greater than the maximum recommended values of 10mg/l. Also this river had high chromophoric dissolved organic matter (CDOM) especially in the dry season where values of up to 326.6 RFU were recorded in wet and 180.7 RFU in dry season (Fig. 3.6 c, d). High values of CDOM indicate higher levels of dissolved organic matter in water. Such high amount of chromophores have affected the aesthetic quality of water to its brown coloured of tea like called in Swahili "Maji ya Chai" hence the name of the river. In addition, high levels of CDOM reflect high levels of fulvic and humic acids in water. Generally the CDOM increased with increase in DO indicating that organic matters responsible for the colour transmissions are in high oxidized states.

The sampling point M2 showed low levels of DO up to **bdl** with absence of aquatic life in water hence a dead river. The amount of DO increased downstream after dilution of oxygen demanding wastes. The highest levels of 8.6 mg/l, 8.7 mg/l and 8.90 mg/l were recorded at M4, M5 and M6 in the wet season with persistence of such levels in the dry season. Despite the brown coloured water, yet it had low turbidity levels in the dry season indicating that most of the coloured substances in water are in its dissolved form in water such as fulvic and humic acids... The highest value of

turbidity was 361.60 NTU recorded at M6 in wet season. Where in the dry season the values were as low as 4.61 NTU recorded at M2. The amount of TSS changed inversely proportionally to its DO and went direct proportional to the DO and COD an indication that TSS are the major contributors to the oxygen demanding wastes in the river. Despite of such variation of TSS its overall amount was quite lower than the WHO recommended values of 5 mg/l.

The nutrient variation in Maji ya Chai River is illustrated in Fig. 7 a, b. Nitrates dominated the pristine environment of the river with low transformation into NH_3 and NH_4^+ . High nitrates levels were recorded at M1 and M2 in both seasons with nitrates levels of 15.9 mg/l and 16.5 mg/l, 22.26 mg/l and 23.10 mg/l in wet and dry seasons, respectively. These levels were lower than the WHO maximum recommended levels for drinking water [15]. The high nitrates values in the pristine environment are contributed by the high nitrogenous wastes produced by wild animals in the Park which most animals spent most of their time along the river. The total soluble phosphate level ranged between 0.05 mg/ to 0.35 mg/l in wet season whereas in the dry season they were between 0.08 mg/l and 0.56 mg/l. Most of these levels were above the recommended values of 0.1 mg/l for the river draining its content to the sea [15]. The levels of total phosphates (TP) ranged between 1.31 mg/l and 11.60 mg/l, 0.15 mg/l and 19.60 mg/l in wet and dry season, respectively. All values in water were higher than recommended.

Higher levels of FC were noted in the floodplain during wet season while in the dry season such levels were noted in the pristine environment. This trend is explained by the fact that in wet season there are many water sources in the river thus animals are evenly distributed for water sources therefore the catchment area is likely to be little affected by wild animals. But in the dry season rivers remain the major source of drinking water, therefore animals are concentrated along the river for water. The pristine environment in this river is entirely in the park while the rest part is in human settlement areas (urban). While animals are drinking water in the rivers they tend to excrete in water source that being the major source for elevated FC in dry season.

Salinity and total hardness remained to be a minor problems in the river in both seasons since very low levels were recorded.

Very high amount of EC and TDS were recorded in the river in both seasons. Maji ya Chai River had the highest levels of EC and TDS among the three rivers. High levels of EC can be caused by high pH as a result of increased level of OH^- ions and presence of high amount of dissolved fulvic and humic acids which are weak electrolytes. Also the high levels of Cl^- and SO_4^{2-} ions as discussed earlier can also account for elevated conductivity of water. During the wet season the conductivity was up to $1187 \mu\text{S}/\text{cm}$ that being recorded at M7 and this amount was elevated to $1722 \mu\text{S}/\text{cm}$ at similar point (Fig. 7 c, d). This value was above the maximum WHO recommended level of $1500 \mu\text{S}/\text{cm}$ [15]. Accordingly, the total dissolved solids (TDS) followed similar trends such that the maximum levels during wet and dry season were $594.00 \text{ mg}/\text{l}$ and $861.00 \text{ mg}/\text{l}$, respectively. These values were within the maximum permissible levels as stipulated by WHO and Australian standards of $600\text{-}1200 \text{ mg}/\text{l}$ [11], [15], [17].

3.4 Dissolved Carbons and Nitrate Sources in Rivers

The stable isotopes of ^{13}C , ^{18}O and ^{16}N for wastewater, ground water, manure, soil composite and plant material in relation to the water sample composition of the rivers were studied to assess their relation in the environment. Since 60-70% of water enters large rivers from first to third order streams, it was necessary to take samples from headwater, middle and a fully developed river (floodplain) of which their differences could also reflect different dissolved organic carbons and nitrates [18]. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ for water in all rivers showed to increase in enrichment downstream which is an indication for increase in evaporation downstream as water temperature also increases (Table 3.4).

3.4.1 Sources of Dissolved Organic Carbons in Rivers

Traces of dissolved organic carbon in water can be detected through their colours if they show a characteristic colour due to chromophoric dissolved organic carbons (CDOM) present in it. Oxidized state of organic carbons can exist as humic and fulvic acids which are chromophoric. Large amounts of these compounds can even change the water

color to a brownish yellow the characteristic experienced by "Maji ya Chai" river which is a translated Swahili language to mean "tea water." Low concentrations of these may not change the aesthetic quality of water.

Water samples from the three rivers were screened for dissolved organic carbons. Maji ya chai river contained the highest levels of dissolved organic carbon of up to $2.31 \text{ mg}/\text{l}$ in the head water (M1). This was expected due to the closeness of the sampling area to the point source of the pollutants which is the foots of Kirurumu hill. Tengeru River showed the concentration range between $0.74\text{-}1.30 \text{ mg}/\text{l}$ where as for Nduruma River the levels were up to $0.20 \text{ mg}/\text{l}$.

The stable isotope studies on various samples around the river showed different origins of dissolved organic carbons (DOC). The stable isotopic signatures of Carbon were measured from water samples and then compared with the stable isotopic signatures of carbon for nearby soil composite, manure, groundwater, plant materials and common fertilizers used by farmers.

Nduruma River showed $\delta^{13}\text{C}$ isotopic signatures of $-20.56 \pm 0.2\text{‰}$ (N6, middle) and $-22.4 \pm 0.22\text{‰}$ (N12, floodplain) whereas the nearby materials had $\delta^{13}\text{C}$ values of $-20.87 \pm 0.2\text{‰}$ (soil composite) and $-22.10 \pm 0.2\text{‰}$ (plant materials) whereas the headwater had dissolved carbon levels below the detection limit (bdl) with other values being as shown in Table 3.4. From these data, the middle water of the rivers showed dissolved carbon originating mainly from soil composite such that the organic carbon incorporated in soil undergo dissolution in water. Occurrence of dissolved organic carbon in the soil composite can happen from leaching of dissolved organic matter into the rain water which pass through the canopy and forest flow and eventually percolate into the soil [19]. A similar pattern occurs for nitrates composition in the soil. The floodplain dissolved carbon showed mainly to originate from plant materials probably dead plant material are swept with water from different points as a result of runoff.

Tengeru River had $\delta^{13}\text{C}$ of $-15.30 \pm 0.2\text{‰}$ (T3, headwater); $-15.47 \pm 0.2\text{‰}$ (T9, middle/human settlement area), $-13.39 \pm 0.2\text{‰}$ (T19, floodplain) and other results are as shown in Table 3.4. These results were also compared with

different nearby common materials and showed $\delta^{13}\text{C}$ of $-15.13 \pm 0.2\text{‰}$ (groundwater); $-15.11 \pm 0.2\text{‰}$ (manure) indicating origin of dissolved organic carbons is from ground water mixing with surface water. In addition, Maji ya Chai had $\delta^{13}\text{C}$ fractionation of $-22.81 \pm 0.2\text{‰}$ (M1, headwater), $-22.23 \pm 0.2\text{‰}$ (M5, human settlement/middle) and $-22.08 \pm 0.2\text{‰}$ (M7, floodplain). All other associated materials showed different fractionation except for plant materials which had $\delta^{13}\text{C}$ fractionation of $-22.10 \pm 0.2\text{‰}$ an indication that the brownish yellow colour of water originates from rotten plant material from the point source of the foots of Kirurumu hill as discussed earlier. The basin of Kirurumu hill is an accumulation centre for most plant material swept from various uphill points which its dead plants stockpiles rot and dissolve with the brownish characteristic colour.

Nduruma river had $\delta^{15}\text{N}-\text{NO}_3^-$ fractionation of $+3.72 \pm 0.3\text{‰}$ (N1, headwater) corresponding to $+3.11 \pm 0.3\text{‰}$ for groundwater meaning that the nitrogen sources were from the ground water containing nitrogen mixing with surface water. The fractionation of $+7.91 \pm 0.3\text{‰}$ and $8.07 \pm 0.3\text{‰}$ (N6, middle/human settlement and N12, floodplain respectively) indicated nitrogen sources from Urea fertilizers applied in farms which showed similar fraction of $+7.95 \pm 0.3\text{‰}$. In such area the farming activities in the steep slopes experienced transportation of soil and dissolved Urea fertilizer to the river. Similar fractionations were depicted by $\delta^{18}\text{O}-\text{NO}_3^-$ indicating similar sources of nitrogen as shown in Table 3.4. Similar comparison technique was used by Aravena *et al* in their study on identification of nitrate from the septic system by comparing the stable isotopes of oxygen and nitrogen from the septic system and the surrounding materials in the environment[20].

Tengeru River showed fractionation of $+8.16 \pm 0.3\text{‰}$ (T3, headwater) which corresponded with $+8.06 \pm 0.3\text{‰}$ for manure meaning that the main source of nitrate in headwater is from animal manure. The results obtained correlate with farming activities around the steep slopes on headwater banks which involve heavy application of cattle manure which are eventually swept off during the wet season due to runoff to the river. The middle/ human settlement and floodplain areas of the river had $\delta^{15}\text{N}-\text{NO}_3^-$ fractionation value of $+9.33 \pm 0.3\text{‰}$ (T9) and $+9.84 \pm 0.3\text{‰}$ (T19), respectively, which corresponded with the fractionation values of soil composite of $+9.02 \pm 0.3\text{‰}$

meaning that the origin of nitrates from those areas are mainly soil incorporated nitrogen/nitrate which can originate from different nitrogen containing matters including living and non living materials.

The headwater of maji ya chai river had fractionation of $+10.46 \pm 0.3\text{‰}$ and the human settlement/middle area of the river showed fractionation of $+10.04 \pm 0.3\text{‰}$ whereas the floodplain area had a fractionation of $+10.37 \pm 0.3\text{‰}$. All areas correspond to nitrate contamination as a result of manure inputs with the fractionation of $+10.12 \pm 0.3\text{‰}$. The source of manure from this river is mainly from wild animals in the Arusha National park since this river is the main source for drinking water in the park thus animals spent most of their time to drink and feed along the river. Meanwhile as the animals feed along the river they excrete within the same area thus their dung and urine are carried along with rainwater in the river.

4 CONCLUSIONS

Monitoring the physicochemical and biological changes of rivers is of profound importance since it tells the immediate measures/remediation to be done to overcome the emerging bad effects. However due to limited resources, a little study on such changes is done after a long period of time. In this study, the physicochemical and biological changes have seen to change downstream in each river due to different environmental conditions the rivers experience. Most parameters are within the WHO maximum permissible levels with a few being above the limits. This includes the fecal coliforms (FC) which were present in all water samples with the headwater of all rivers having low amount compared with the middle /human settlement and floodplain areas. Increase in FC in those areas is mainly caused by different human activities such as uncontrolled littering and poor hygiene/management of domestic wastes. Farming activities along the river with steep slopes is also another factor which causes increase of turbidity and nutrients loading due to runoff of rain water. Farming activities in such areas should be stopped to preserve the riparian environment of the river as per the Tanzania environmental conservation law which requires conserving a buffer zone of 60 meters from each side of the river bank [21] for its sustainability and which in turn will act as good buffer for different environmental changes near the river banks.

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