# Use of physicochemical parameters and metal concentrations in assessing anthropogenic influences on coastal rivers in Dar es Salaam, Tanzania

Zakaria Mhande<sup>1,2</sup>, Matobola J. Mihale<sup>1</sup>, Harieth Hellar-Kihampa<sup>1\*</sup>

<sup>1</sup> Faculty of Science, Technology and Environmental Studies, The Open University of Tanzania, PO Box 23409, Dar es Salaam, Tanzania <sup>2</sup> Tanzania Bureau of Standards, PO Box 9524, Dar es Salaam, Tanzania \* Corresponding author: hhellar@yahoo.co.uk

# Abstract

Spatio-temporal variations in water quality of three rivers along the Indian Ocean coast in Dar es Salaam, Tanzania, were investigated based on physicochemical parameters and metal concentrations. A compliance analysis was performed based on the Tanzania Bureau of Standards (TBS) and World Health Organization (WHO) limits to examine the suitability of water for domestic use. The dataset was subjected to statistical analysis to determine differences and similarities amongst the rivers. Levels of pH (6.83-11.41), total dissolved solids (203–34,333 mg/L), electrical conductivity (9,408-68,014 µS/cm), turbidity (10.0-45.0 NTU), chloride (108-14,248 mg/L), sulphate (35-766 mg/L) and ammonium (40-5,468 µg/L) complied with neither TBS nor WHO limits. Dissolved oxygen (1.4-6.6 mg/L), chemical oxygen demand (91-1,863 mg/L), total suspended solids (11.9-50.7 mg/L), alkalinity (200-2,658 mg/L), total hardness (362-12,1312 mg/L), salinity (0.19-29.35 ppt) and phosphate (<method detection limit-3.01 µg/L) indicated polluted water in parts of the rivers. Pb (0.7-24.0 µg/L) exceeded both the TBS and WHO limits, whereas Cr, Cu, Fe, Zn and Cd were below limits. Water quality was poorer during the wet season. The results indicate that water from the rivers is unsafe for human consumption and the poor water quality probably also affects the ecology of the rivers. Strategic measures to protect the rivers from further contamination are suggested.

**Keywords:** water quality, physicochemical parameters, metal concentrations, coastal rivers, anthropogenic impacts, Tanzania

# Introduction

The coastal area of Tanzania contains numerous resources associated with coral reefs, mangroves, seagrass beds, sand banks, wetlands, beaches and estuaries (Masalu, 2000). These resources and habitats provide life support to coastal communities through activities such as fishing, aquaculture and tourism that play an important role in social and economic development of the coastal region (Francis and Bryceson, 2000). The area is also endowed with freshwater resources, including rivers and streams that are used for different human activities. Moreover, in some locations, the river waters are used for irrigation in urban vegetable farming that is commonly conducted along the riverbanks (Sibomana *et al.*, 2012; Mhache and Lyamuya, 2019). Growing coastal populations and emerging anthropogenic sources of pollution such as industrial effluents, urban runoffs, agricultural fields and solid waste dumps are exerting increasing pressure on the fresh and marine water quality of the area (Mihale, 2017). The effects have been investigated by several researchers, who revealed detectable levels of various contaminants, including pesticide residues (Mwevura *et al.*, 2002), polycyclic aromatic hydrocarbons (Gaspare *et al.*, 2009), metals (Mihale, 2021), nutrients and bacteria (Nyanda *et al.*, 2016), and assortments of inorganic compounds such as residual acids, suspended solids, oils, greases and textile dyes, particularly from the discharge of unsuitably treated industrial wastewaters (Kihampa *et al.*, 2016). Furthermore, the coastal rivers of Dar es Salaam city have been reported to receive large quantities of solid wastes that are dumped directly into the rivers in commercial and residential areas, significantly contributing to water pollution (Bubegwa, 2012).

Physicochemical properties of water are key factors in evaluating its quality and suitability for various uses and its ability to sustain aquatic life. Due to the ease of their determination and interpretation, these parameters present a suitable means for the initial understanding of water characteristics, including any undesirable properties or possible health effects (WHO, 2011). Along with these, there are various chemical species of concern whose presence or enrichment in water quality monitoring are well known, e.g., nutrients and trace metals. For example, several metals have been identified as chemicals of significant public health concern by the WHO, although some of them, like Fe, Cu, Zn are beneficial to human health at permissible concentrations (WHO, 2011).

Owing to the ecological importance and the socio-economic significance of the rivers along the Indian Ocean coast in Dar es Salaam city, and considering their ever-changing dynamics, it is of paramount importance to periodically monitor the quality of their waters so as to identify changes in the underlying conditions. This study is one of such endeavors, in which concentrations of some physicochemical parameters, ionic species and selected metals are quantified in three the rivers of Kizinga, Msimbazi and Mbezi. To assess the extent to which the water quality has been affected, the levels are compared to the guidelines for such variables in potable waters set by the WHO (2011) and the Tanzania Bureau of Standards (TBS, 2008). Statistical analyses are used to highlight the observed concentrations in association with seasonality and land-use practices. The aims of the study were to examine trends in spatial and temporal variations, elucidate possible sources of contamination, provide insight into the current water quality status of the rivers and identify hotspots that may need closer monitoring.

# Materials and Methods

# The study area

Dar es Salaam city is located at 6°48' South and 39°17' East, on the coast of Tanzania. The total surface area of the city is about 1,800 km<sup>2</sup>, comprising of about 1,400 km<sup>2</sup> of land mass (NBS, 2019). The city had a population of 4,364,541 according to the 2012 census and an intercensal growth rate of 5.6%. The population in 2021 is thus estimated at 6,015,000. Due to its proximity to the equator and the Indian Ocean, the city experiences tropical climatic conditions characterized by hot and humid weather through much of the year. The average annual precipitation is around 1100 mm (Mtoni et al., 2012). December and January have an average precipitation of up to 195 mm, while in July and August it is much lower, up to 47 mm. The area, like many other parts of the country, has distinct rainy and dry seasons; the long rain season between March to May, followed by several months of dry season around June to September (Mahongo and Francis, 2012). River flows in the Dar-es-Salaam area is mainly controlled by the precipitation rate, and are normally high during the rainy season (up to 15 m<sup>3</sup>/s) and low during the dry season (1 m<sup>3</sup>/s or lower) (Van Camp et al., 2013).

This study considered three rivers, namely the Kizinga, Mbezi and Msimbazi, that run through Dar es Salaam city towards the coast. The Kizinga River (about 30 km long) flows through the urbanised areas of Mbagala, Buza, Chang'ombe, Keko, Mtongani and Kurasini and through the Mtoni mangroves and over a mudflat before draining into the Indian Ocean. As a result, it is expected to collect mixed wastes from households, agriculture, industries, and car and truck washing activities along its catchment (Kruitwagen et al., 2008). The Msimbazi River flows for about 36 km from the Kisarawe hills to the shores of the Indian Ocean, passing through highly populated and industrialized areas. Along its course it receives different industrial (dye, textiles, soap and detergent, breweries, building material and food), agricultural (fertilizers and pesticides) and household wastes. The Mbezi River is the shortest of the three, about 24 km long, flowing through the less populated areas of Kawe, Mbezi Beach and other nearby areas on the western side of the city, and discharges into the Indian Ocean. Along its course, the Mbezi River passes through fewer industrial areas but more human settlements that generate household wastes and sewage discharges (Mhina et al., 2018).

# Sample collection

Water samples were collected from fifteen stations, five on each river. Figure 1 is a map of Dar es Salaam, indicating the sampling locations in the three rivers.

Table 1 gives the code names and position descriptions of the sampling locations. Two sampling campaigns were conducted in March to April 2018 for the wet season and another two in August to September 2018 for the dry season. Samples were collected from the side of the riverbanks at the same spots during the two campaigns, as identified by a hand-held global positioning system (GPS).

were acidified after collection to pH < 2.0 using 5 mL concentrated  $HNO_3/L$ . All sample bottles were placed in ice-cases at <10 °C and transported to the Analytical Chemistry Laboratory at the Chemistry Department of the University of Dar Salaam for analyses.

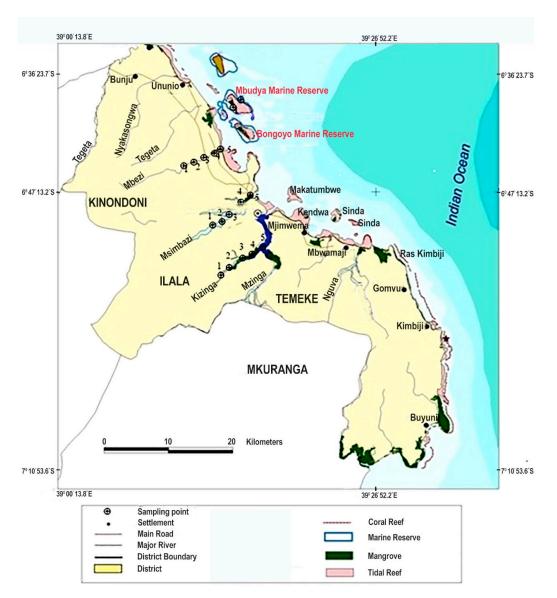


Figure 1. Map of Dar es Salaam showing the sampling locations along the three rivers.

To collect the samples, clean pre-labelled Teflon capped plastic bottles (1 litre) were vigorously rinsed twice and filled with river water at each station. Field parameters were measured and recorded on site. Two water samples were taken at each station, one for the determination of the conventional physicochemical parameters in the laboratory and the other for analysis of metals. Water samples for metal determination

### Sample Analysis

Water samples were analysed for a total of twenty-one parameters, i.e., fourteen physicochemical parameters (pH, total dissolved solids (TDS), electrical conductivity (EC), total suspended solids (TSS), turbidity, dissolved oxygen (DO), chemical oxygen demand (COD), alkalinity, total hardness, salinity, chloride (Cl-), sulphate ( $SO_4^{2-}$ ), phosphate ( $PO_4^{3-}$ ) and ammonium

River	Station Code	GPS C	Elevation (Meters)	
	Kz <sub>1</sub>	S 06°53.060′	E 039°15.853'	8
	Kz <sub>2</sub>	S 06°52.987	E 039°16.176'	6
Kizinga	Kz <sub>3</sub>	S 06°52.903'	E 039°16.521'	8
	$Kz_4$	S 06°52.439′	E 039°17.054′	4
	Kz <sub>5</sub>	S 06°52.107	E 039°17.485′	4
	Ms <sub>1</sub>	S 06°49.125′	E 039°15.318′	10
	$Ms_2$	S 06°48.943′	E 039°15.764'	12
Msimbazi	Ms <sub>3</sub>	S 06°48.592′	E 039°15.921'	7
	$Ms_4$	S 06°48.236′	E 039°16.171'	11
	$Ms_5$	S 06°47.775′	E 039°16.849'	3
	Mz <sub>1</sub>	S 06°4.098′	E 039°1.020'	25
	$Mz_2$	S 06°42.728′	E 039°13.689'	8
Mbezi	$Mz_3$	S 06°42.715′	E 039°13.901'	6
	$Mz_4$	S 06°42.696	E 039°13.967	6
	$Mz_5$	S 06°42.592'	E 039°13.984'	7

Table 1. Description of the sampling sites.

 $(NH_4^+)$ , and seven metals (Al, Cr, Cu, Fe, Pb, Zn and Cd). Five parameters (pH, TDS, EC, turbidity and DO) were measured *in-situ* by hand-held portable water-quality instruments and their results recorded on site, whereas the rest of the parameters were analyzed in the laboratory upon arrival.

The measurements of pH, EC and TDS were done by a low range combo® pH/EC/TDS meter (Model HI 98129, HANNA Instruments Inc., USA) which measures the three parameters simultaneously. Calibration was done as per the manufacturer's instructions, using the manufacturer-supplied pH standard buffer solutions of pH 4.01, 7.01 and 10.01, and the conductivity standard 1413 µS/cm. Dissolved oxygen was measured by a digital DO meter (Model HI 98186, HANNA Instruments Inc., USA), which was calibrated as described in the manufacturer's manual. Turbidity was measured using an electronic turbidity meter (nephelometer) (Model HI 98713, HANNA Instruments Inc., USA) that utilizes the principle of light scattering to measure turbidity in terms of nephelometric turbidity units (NTU). Measurements involved calibration of the meter with the manufacturer's supplied turbidity standards.

The analysis of TSS was done by the filtration process, Standard Method 2540 D (APHA/AWWA/WEF, 2017). In this method, 250 ml water samples were filtered on pre-weighed Whatman® glass microfiber filters (2.0 µm particle retention) and the filters dried at 105 °C for 2-3 hours, then re-weighed to determine the weight change, which corresponded to the TSS content expressed in mass per volume of sample filtered (mg/L). The analysis of COD was done by the open reflux method, Standard Method 5220 B (APHA/ AWWA/WEF, 2017), in which the organic matter in the sample (20 mL) was oxidized by refluxing in a mixture of concentrated H<sub>2</sub>SO<sub>4</sub>, 0.25N solution of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, and dried powders of Ag<sub>2</sub>SO<sub>4</sub> and HgSO<sub>4</sub> for 2 hours on a heating mantle. The mixture was then titrated against standardized ferrous ammonia sulphate (FAS) solution with ferroin solution as an indicator. Finally, COD was calculated as mg of O<sub>2</sub> per mL of sample. Total hardness was determined by the Ethylene-diamine-tetra-acetic acid (EDTA) titrimetric method, i.e., Standard Method 2340 C (APHA/AWWA/WEF, 2017), in which 25 mL of water sample added with 1 mL of ammonia buffer reagent was titrated against EDTA solution using Eriochrome Black T indicator. Total hardness was then calculated as mg (CaCO<sub>3</sub>)/ mL sample. Alkalinity was determined by the titration method, Standard Method 2320 B (APHA/AWWA/ WEF, 2017), in which 10 mL water sample was titrated against a standardized H<sub>2</sub>SO<sub>4</sub> solution using phenolphthalein and methyl orange as indicators. The total volume of titrant was used to estimate the alkalinity of the sample. Salinity was determined by the conductivity method, Standard Method 2520 B (APHA/ AWWA/WEF, 2017). Phosphate (PO<sub>4</sub><sup>3-</sup>-P) was determined by the ascorbic acid method, Standard Method 4500-P E (APHA/AWWA/WEF, 2017), which involved

treating water samples (50 mL) with ammonium molybdate and potassium antimony tartrate, which react with any orthophosphate present in the sample to form an antimony-phosphate-molybdate complex. This was then reduced by ascorbic acid, and the resulting colour intensity was measured spectrophotometrically using an Ultraviolet-Visible (UV) spectrophotometer at 880 nm. Sulphate was determined as SO42- ions using the turbidimetric method, Standard Method 4500-SO42- E (APHA/AWWA/WEF 2017), which is based on the principle of conversion of the  $SO_4^{2-}$  ion to barium sulfate (BaSO<sub>4</sub>) under controlled conditions. In the procedure, about 50 g of BaCl<sub>o</sub> crystals were added to a 50 mL filtered water sample which contained a buffer solution prepared as per the description in the method. The resulting solution was then stirred for one minute and thereafter its absorbance was determined by a spectrophotometer at 420 nm. The SO<sup>2-</sup> concentration was calculated by comparison with standard curves.

Chloride ion (Cl<sup>-</sup>) was determined by the argentometric method, Standard Method 4500-Cl<sup>-</sup> B (APHA/ AWWA/WEF, 2017), in which a 50 mL water sample was directly titrated using  $K_2CrO_4$  indicator against standardized AgNO<sub>3</sub> titrant until a yellow-colored solution was converted to a persistent brick red colour. The concentration of  $NH_4^+$  was determined by the phenate method, Standard Method 4500-NH<sub>3</sub>-F (APHA/AWWA/WEF, 2017). In the procedure, 20 mL of water sample in a 25 mL volumetric flask was added with 2 mL of phenol-nitroprusside solution, followed by 2 mL of alkaline hypochlorite solution and distilled water to make 25 mL of solution. The absorbance of the sample was recorded on a spectrophotometer at 635 nm.

Metals were analyzed instrumentally by Flame Atomic Absorption Spectrometry (FAAS) (iCE3000 SERIES, Thermo Scientific) using standard method 3111A as described in APHA/AWWA/WEF (2017). For each metal determined, the instrument was calibrated using working standards for different elements at different concentrations prepared in 5 % (v/v) HCl. The calibration curves that aid to estimate concentration of the intended analyte were made for each element. Determination of each element was achieved at specific wavelength, such as 309.2 nm for Al, 228.7 nm for Cd, 324.7 nm for Cu, 357.8 nm for Cr, 248.3 nm for Fe, 216.9 nm for Pb, and 213.8 nm for Zn. The detection levels were as described in the specific method (APHA/AWWA/WEF (2017).

### **Quality Assurance and Control**

The quality of the analytical data was assured in all steps of the study, i.e., from sample collection, transport, laboratory analysis, and finally data checks. In the sampling procedure, all tools were thoroughly cleaned and rinsed with distilled water, and the instruments were calibrated using prescribed protocols by the instruments' manufacturers. Samples were carefully handled by ensuring correct labelling of the sample bottles, packaging and transporting of the samples to the laboratory. In the laboratory, the quality of analysis was assured by analyzing samples of distilled water as blank samples. After ensuring that the blank samples were free of the target analytes, they were spiked with standard solutions of the analytes at their method detection limits and processed by the same method as used for the ordinary samples, as described in the respective methods. The data checks for all field and laboratory measurements were done by ensuring that the obtained results were within the expected ranges of a particular parameter, that they were physically and scientifically possible, and that they were within the detection limits of the method used.

### **Data Analysis**

The datasets were tested for normality using the Shapiro-Wilk test, in which a null hypothesis that a variable is normally distributed was rejected if p < 0.05. Descriptive statistics were used to summarize results for concentration ranges, means and standard deviations. The seasonal variation trends were studied using the Wilcoxon Signed Ranks test for paired samples, in which the difference in the measured values between the two seasons was tested for statistical significance at the 95 % confidence level. The Friedman test for multiple related samples was employed to compare levels of the measured parameters among the three rivers. The dataset was further subjected to Spearman Rank correlation analysis for non-normal data to evaluate the relationships among the measured parameters. Factor reduction using Principal Component Analysis (PCA) with Varimax rotation was used to reduce the large dataset to a small number of new variables that could account for at least 75 % of the total variance and explain the overall associations among the measured parameters. Those with eigenvalues  $\geq$  1.0 were considered significant. Hierarchical Cluster Analysis (HCA) was used in characterizing the different sampling locations to assess the similarities and differences among them and identify possible patterns of the measured parameters. All statistical analyses were carried out using the statistical package IBM SPSS Statistics 23.0.

Deveneter	Wet seaso	n (n = 15)	Dry seaso	TRO	WHO	
Parameter -	Range	Mean ± SD	Range	Mean ± SD	TBS	WHO
pН	7.44 - 11.41	8.28 ± 1.08	6.83 – 9.13	$7.92 \pm 0.53$	5.5 - 9.5	6.5 - 9.2
TDS (mg/L)	252 - 34333	$9077 \pm 12882$	203 - 30236	$7860 \pm 11457$	1500	1000
EC (µS/cm)	500 - 68014	$17982 \pm 25520$	408 - 61205	$17038 \pm 23701$	2500	2500
TSS (mg/L)	12.8 - 50.7	$28.1 \pm 11.9$	11.9 – 34.7	$22.1\pm7.1$	-	-
Turbidity (NTU)	10.8 - 45.0	$23.7\pm10.9$	10.0 - 29.2	$18.9\pm6.61$	5	< 5
DO (mg/L)	1.4 - 6.6	$4.3 \pm 1.7$	2.6 - 6.4	$4.9 \pm 1.1$	-	-
COD (mg/L)	105 - 1863	$725\pm590$	91 - 1774	$649\pm523$	-	
Alkalinity (mg/L)	200 - 2658	$611 \pm 625$	207 - 1145	$461 \pm 269$	-	500
Total Hardness (mg/L)	473 - 101333	$21890 \pm 30412$	362 - 121312	23913 ± 37104	600	500
Salinity (ppt)	0.19 - 25.70	$7.76 \pm 9.97$	0.21 - 29.35	$7.47 \pm 10.38$	-	
Chloride (mg/L)	108 - 14248	$4228\pm5571$	114 - 16245	$4137\pm5745$	250	
Sulphate (mg/L)	42 - 766	$273 \pm 258$	35 - 723	$254\pm239$	400	500
Phosphate (µg/L)	ND – 2.74	$1.31 \pm 1.11$	ND - 3.01	$1.07 \pm 1.00$	-	
Ammonium (µg/L)	90 - 5468	$1432 \pm 1581$	40 - 2131	$585 \pm 611$	500	

Table 2. Concentration ranges, means and standard deviations (n = 30) of the measured water quality parameters in the rivers.

# Results and discussion

# Physicochemical parameters

Descriptive data for measured water quality parameters at the fifteen stations during the two seasons are summarized in Table 2. The physicochemical quality of water was assessed based on a comparison to limits for potable water provided by the TBS (TBS, 2008) (TZS 789: 2008) and WHO (WHO, 2011). The normality test showed that all parameters were not normally distributed, due to the presence of extreme values.

Figures 2(a) and 2(b) depict the variation in trends for mean values for each parameter as measured at individual sampling stations.

The results of Spearman rank correlation analysis used to evaluate associations between pairs of measured parameters at the 15 stations are summarized in Table 3.

The data show that the river waters were near neutral to alkaline, with a pH ranging between 7.44 - 11.41 (8.28 ± 1.08) during the wet season and 6.83 - 9.13 (7.92 ± 0.53) during the dry season (Table 2). The pH of freshwater is an important parameter as it reflects on the state of pollution and productivity of the water. The Tanzanian pH limit for potable water is 5.5 - 9.5, whereas the maximum permissible limits for potable water according to the WHO is 6.5 - 9.2 (Table 2). The typical values for natural river and stream water are said to range from 4 to 11 (Chapman and Kimstach, 1996). Figure 2a shows that the lowest pH

was recorded at the Mbezi River station Mz<sub>9</sub> and the highest pH of 11.41 was recorded at Msimbazi River at station Ms, during the wet season. This station, which is upstream and close to presumed pollution sources, has a pH that exceeds the maximum permissible limits for both the national and WHO limits. Generally, all the Msimbazi River stations were found to have a relatively higher pH compared to the other rivers. For the Mbezi and Kizinga Rivers, the pH was within the WHO and TBS limits. When data from the three rivers were subjected to the Friedman test, a statistically significant difference was confirmed based on their median ranks i.e., Msimbazi River (8.45), Kizinga River (7.88), Mbezi River (7.87), ( $\gamma^2(2) = 8.600$ , p = 0.014). This could be an indication of inputs of compounds that make the water more alkaline in this river, given its surroundings and the human activities taking place around its banks. The pH was positively correlated with TSS, turbidity and alkalinity, as shown in Table 3. Studies have indicated that waters that have moderate to high levels of total alkalinity (> 50 mg/L)) usually have neutral to slightly basic pH (Nagwa, 2016). This is clearly depicted in this study where alkalinity was higher than 200 mg/L and pH higher than 6.8.

The TDS concentrations ranged between 252 - 34,333 mg/L during the wet season and 203 - 30,236 mg/L during the dry season (Table 2). The acceptable TBS limit of TDS in potable water is 1,500 mg/L while that of the WHO is 1,000 mg/L (Table 2). Both these limits were exceeded at about 50 % of the stations during both seasons, e.g., Kz<sub>4</sub>, Kz<sub>5</sub>, Ms<sub>1</sub>, Ms<sub>5</sub>, Mz<sub>4</sub>, MZ<sub>4</sub> and Mz<sub>5</sub>.

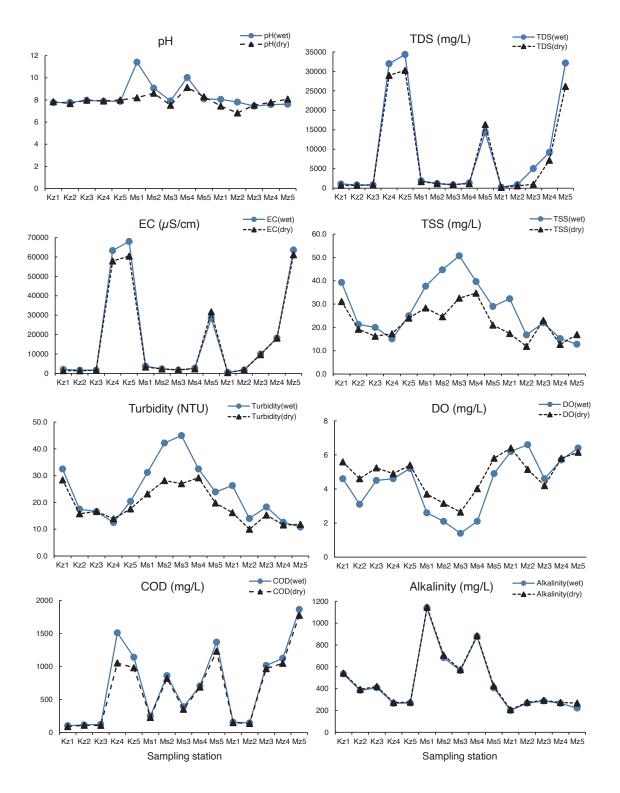


Figure 2(a). Variations of the mean values of pH, TDS, EC, TSS, Turbidity, DO, COD, and Alkalinity in the study area during the two seasons.

The highest concentrations during both seasons were measured at station  $Kz_5$  followed by station  $Kz_4$  (Fig. 2a). The high TDS concentration observed at these locations that are correlated to salinity may be due to saltwater intrusion (Anhwange *et al.*, 2012). The levels

recorded in the three rivers in this study exceed by 30-fold the TBS permissible limit, which indicated significant deterioration of water quality. Based on the Friedman test results, the Kizinga River was found to have the highest TDS concentrations.

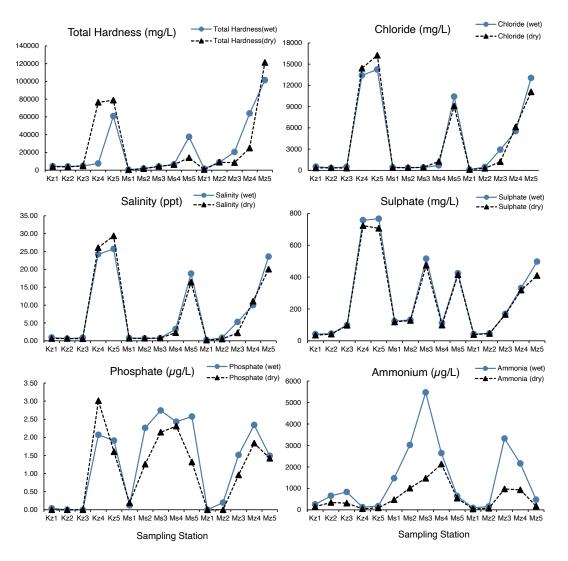


Figure 2(b). Variation of the mean values of Total Hardness, Chloride, Salinity, Sulphate, Phosphate, and Ammonium in the study area during the two seasons.

The ranges of EC recorded in this study were 500 -68,014 µS/cm and 408 - 61,205 µS/cm during the wet and the dry seasons respectively (Table 2). These concentrations also significantly exceed both the national (TBS) and the WHO limits of 2,500 µS/cm in most of the locations as well as the normal range of EC in natural river waters, which is expected at 50 - 1500 µS/cm (Patil et al., 2012). The highest concentrations were recorded at  $Kz_4$  followed by  $Kz_5$  and  $Mz_5$  (Fig. 2a). The high EC concentrations probably reflect saltwater intrusion. Researchers have established that EC and TDS are highly positive correlated because the conduction of electric current primarily depends on the concentration of ionic species, and that EC values are almost usually twice those of TDS (Siosemarde et al., 2010). The same pattern was observed in this study (Fig. 2a). TDS and EC were highly correlated (r = 0.977) as shown in Table 3. As expected, both TDS and EC were positively correlated with COD, total hardness, Cl<sup>-</sup>, salinity, SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> (Table 3).

Total suspended solids (TSS) are particles of organic or inorganic nature that are larger than 2 microns found in the water column, anything smaller than that is considered a dissolved solid (Chapman and Kimstach, 1996). The concentrations of TSS recorded in this study were 12.8 – 50.7 mg/L during the wet season and 11.9 – 34.7 mg/L during the dry season (Table 2). The highest concentrations were measured at Ms<sub>3</sub> followed by Ms<sub>2</sub> and Ms<sub>4</sub> (Fig. 2a). The Friedman test showed the Msimbazi River to generally have the highest levels of TSS compared to the other rivers, with median ranks of Msimbazi River (33.65), Kizinga River (20.65), Mbezi River (16.85) ( $\chi^2(2) = 9.800$ , p = Table 3. Spearman Rank correlation matrix between pairs of water quality parameters (n = 30).

	рН	TDS	EC	TSS	Turb.	DO	COD	Alkal.	T. Hard.	Cl	Salin.	<b>SO</b> <sub>4</sub> <sup>2-</sup>	PO <sub>4</sub> <sup>3-</sup>	$\mathbf{NH}_{4}^{+}$
рН	1.000													
TDS	0.243	1.000												
EC	0.149	0.977**	1.000											
TSS	0.485**	-0.132	-0.206	1.000										
Turb.	$0.532^{**}$	-0.176	-0.277	0.960**	1.000									
DO	-0.318	0.106	0.143	-0.642**	-0.621**	1.000								
COD	0.137	0.861**	0.890**	-0.216	-0.287	0.187	1.000							
Alkal.	0.541**	-0.128	-0.190	0.679**	0.736**	-0.767**	-0.313	1.000						
T. Hard.	-0.208	0.666**	0.725**	-0.490**	-0.556**	0.472**	0.673**	0.502**	1.000					
CI⁻	0.096	0.920**	0.918**	-0.187	-0.263	0.181	0.804**	-0.232	0.800**	1.000				
Salin.	0.107	0.923**	0.917**	-0.180	-0.254	0.175	0.803**	-0.227	0.799**	0.999**	1.000			
SO4 2-	0.101	0.827**	0.828**	-0.083	-0.147	-0.062	0.839**	-0.139	0.605**	0.798**	0.797**	1.000		
PO <sub>4</sub> <sup>3–</sup>	0.235	0.650**	0.616**	0.218	0.162	-0.255	0.697**	0.091	0.464**	0.651**	0.658**	0.760**	1.000	
$\mathbf{NH}_{4}^{+}$	0.216	0.078	0.045	$0.440^{*}$	$0.454^{*}$	-0.651**	0.134	0.562**	-0.136	0.017	0.020	0.167	$0.425^{*}$	1.000

\*\*. Correlation is significant at the 0.01 level (2-tailed).

\*. Correlation is significant at the 0.05 level (2-tailed).

0.007). One of the common sources of TSS in rivers is soil erosion along the riverbanks, particularly caused by human activities (Rossi *et al.*, 2006). The Msimbazi River banks are prone to erosion from vegetable farming taking place around them, especially during the rainy season. The TSS levels were found to positively correlate with alkalinity (Table 3).

Turbidity is a measure of the relative clarity of water that indicates the level of suspended and colloidal matter, such as clay, silt, finely divided organic and inorganic matter and microscopic organisms that may interfere with the passage of light through the water (Awoyemi et al., 2014). The turbidity values recorded in this study were 10.8 - 45.0 NTU during the wet season and 10.0 - 29.2 NTU during the dry season. The limit set by both the WHO and TBS for turbidity in potable water is 5 NTU (Table 2). This was exceeded in all fifteen locations during both seasons. Turbidity and TSS measure approximately the same water quality property except that TSS provides an actual weight of the particulate material present in the sample (Araoye, 2009). The two parameters are often highly positively correlated as was also observed in this study (r = 0.960; Table 3). As was observed for the TSS concentrations, the Msimbazi River had the highest levels of turbidity, probably due to the same reasons of human activities such as vegetable farming that are taking place along the river banks.

Dissolved oxygen is an important water quality parameter since it is required for the maintenance of

aerobic conditions in the water column. It is one of the major parameters of interest in water quality assessment in this study because it indicated changes in physical, chemical, and biological processes induced by both natural and anthropogenic activities within the water. Water is considered generally healthy when its DO range is 6.5 - 8.0 mg/L and 80 - 120 % saturation (Araoye, 2009). Data collected in this study indicated DO concentration ranges of 1.4 - 6.6 mg/L and 2.6 - 6.4 mg/L during the wet and dry season respectively. This showed depletion of the DO concentration at some locations, such as Ms<sub>1</sub>, Ms<sub>2</sub>, Ms<sub>3</sub> and Ms<sub>4</sub> (Fig. 2a). Among the reasons for low DO concentration in a body of fresh water is decomposition of organic matter (Araoye, 2009). The decrease in DO was also found to correlate with increase in TSS and turbidity (Table 3). The Friedman test showed that the Msimbazi River generally had the lowest concentrations of DO compared to the other rivers. This continues to assert the earlier suggestion of the possibility of relatively higher pollution load in the Msimbazi River compared to the other rivers.

The data gathered in this study indicated COD ranges of 105 - 1,863 mg/L and 91 - 1,774 mg/L during the wet and the dry season respectively. The COD measurements in natural river water is used to indicate the quantity of oxygen required to chemically oxidize organic contaminants in water into inorganic end products (Khan and Ali, 2018). It is useful for measuring human impact on water quality of rivers. The COD concentrations in surface water resources is expected to typically range from 20 mg/L or less in unpolluted waters to greater than 200 mg/L in waters receiving wastewater effluents (Chapman and Kimstach, 1996). The high COD concentrations exceeding 1,000 mg/L measured in some locations (Table 2) indicate that the rivers are generally impacted by organic wastes from human activities, likely to be from discharges of sewage and wastewaters. A study by Mihale et al. (2021) observed that sewage is an important anthropogenic source impacting the coastal rivers in this region. Furthermore, vegetable farming activities along the Msimbazi River could be producing organic wastes due to application of organic manure. The levels of COD were found to be positively correlated with TDS, EC, total hardness, Cl-, salinity, SO<sub>4</sub><sup>2–</sup> and PO<sub>4</sub><sup>3–</sup> (Table 3).

Alkalinity levels measured in this study ranged between 200 - 2,658 mg/L during the wet season and 207 – 1,145 mg/L during the dry season. Measuring the alkalinity of a freshwater body is important in determining its ability to neutralize acidic pollution from different sources such as acid rainfall, wastewaters, and agricultural practices. It is one of the best measures of the sensitivity of the river to acid inputs and its buffering capacity or resistance to pH changes upon the addition of acids or bases (Patil et al., 2012). Although alkalinity has no known adverse health effects, its levels affects the palatability of water and its suitability to piping and use for domestic purposes (EWURA, 2020). The alkalinity of natural waters is primarily due to the presence of weak acid salts such as bicarbonate, although strong bases such as OH- may also contribute in extreme environments. Normal river water is expected to have an alkalinity ranging between 100 and 250 mg/L (Mattson, 2014). The WHO set a permissible limit of 500 mg/L for drinking water (Table 2). This level was exceeded in a few locations, particularly in the Msimbazi River (Fig. 2a), probably due to inputs of alkali-inducing materials such as soap and detergent residues from industries along its catchment. The strong negative correlation with DO indicates respiration of organic matter as another source of increased alkalinity due to the production HCO<sub>3</sub>, which has a potential of making the system highly heterotrophic. In this case high alkalinity is not a sign of good health for river water (Nyanda et al., 2016). Alkalinity was also positively correlated to total hardness (Table 3), an association that has been established in other studies (e.g., Boyd et al., 2016).

The total hardness measured in the three rivers in this study ranged from 473 – 101,333 mg/L during the wet

season, and 362 - 121,312 mg/L during the dry season. Total hardness and alkalinity are often related because the main source of alkalinity is usually from carbonate rocks (limestone) which are mostly CaCO<sub>3</sub> (Boyd et al., 2016). However, hardness in water is not caused by a single substance but by a variety of dissolved metallic ions, predominantly Ca2+ and Mg2+, although other cations such as aluminium, barium, iron, manganese, strontium, and zinc, mostly from natural sources, may also contribute (WHO, 2010). The WHO potable water limit for total hardness is 500 mg/L, whereas the TBS limit is 600 mg/L (Table 2). Hard water is not a health hazard: in fact, some researchers have investigated the potential beneficial health effects of low levels of hardness in drinking water (Ong et al., 2009). However, the levels measured in some locations in this study e.g.,  $Kz_5$ ,  $Ms_5$ , and  $Mz_5$ , exceed the beneficial level.

Chloride occurs naturally at low concentrations in freshwater bodies, such as the three rivers in this study. The main source is dissociation of salts, such as NaCl or CaCl<sub>9</sub>, in water (Berger, 2019). The data obtained revealed chloride concentrations of 108 - 14,248 mg/L during the wet season and 114 - 16,245 mg/L during the dry season. Chloride levels in unpolluted river waters are expected to be below 40 mg/L and usually in the range 15 - 35 mg/L for rivers and other freshwater bodies (Alam et al., 2007). The WHO sets a maximum limit of 250 mg/L chloride in drinking water. This value was exceeded at all stations except Mz<sub>1</sub>. An increase in chloride concentration at levels above 250 mg/L will begin to make water taste salty (EWURA, 2020). The high chloride levels indicate inputs from the sea (sea water infiltration), particularly for the stations located close to the ocean, such as Kz<sub>5</sub>, Mz<sub>5</sub>, and Ms<sub>5</sub>.

Salinity measured in the three rivers ranged from 0.19 -25.70 ppt during the wet season, and 0.21 - 29.35 ppt during the dry season, with means of 7.76 ppt and 7.47 ppt respectively. Fresh water from rivers is expected to have 0.5 ppt or less of salinity, produced by natural processes such as weathering of rocks and rain deposits. These small amounts of dissolved salts are vital for the life of aquatic plants and animals. However, the salinity levels measured in these locations can be considered normal and natural for rivers connected to the oceans in estuarine systems (Berger et al., 2019). The highest concentrations of both chloride and salinity were measured in samples from Kizinga River (Fig. 2b), particularly at stations  $Kz_4$  and  $Kz_5$ , probably due to their proximity to the ocean. Salinity and Cl- followed the same spatial trend as shown in Fig. 2(b).

The two parameters are highly positively correlated (r = 0.999) as shown in Table 3, because salinity is measure of the total salt concentration, comprised mostly of Na<sup>+</sup> and Cl<sup>-</sup> ions, whereas Cl<sup>-</sup> come from the dissociation of salts, such as NaCl in water (Berger *et al.*, 2019).

Sulphates occur naturally in numerous minerals and are used commercially, principally in the chemical industry. They may be discharged into water in industrial wastes and through atmospheric deposition (WHO, 2003a). Sulphate levels measured in the three rivers in this study ranged from 41.7 to 766.2 mg/L during the wet season and 35.3 to 722.9 during the dry season. Both the WHO and TBS limits of sulphate in potable water (Table 2) were exceeded at some locations in the Kizinga and Msimbazi Rivers (Fig. 2b). The highest concentrations during both seasons were measured at Kz4 and Kz5. Seawater may have contributed to sulphate levels at some locations. However, the high sulphate concentration at the two stations are outliers and alluded to a point source, probably sewage treatment plants and industrial discharges from textile mills around the area. However, most of the other stations had rather low levels of sulphates. Noticeable changes in water taste are said to occur in concentrations exceeding 250 mg/L (WHO, 2003a), therefore water at locations  $Kz_4$ ,  $Kz_5$ ,  $Ms_5$  and  $Mz_5$  that have sulphate levels exceeding this concentration may be affected.

Concentrations of phosphate ( $PO_4^{3-}-P$ ) were found to range from below the method detection limit to 3.01 µg/L. Phosphate is rarely found in high concentrations in fresh waters since it is actively taken up by plants, and its concentration in natural river waters is expected to range from 0.005 to 0.05 mg/L (Chapman and Kimstach, 1996). The phosphate concentrations in this study were well below this level at all sampling locations, but were the highest at Msimbazi River stations, especially during the wet season, probably due to run-off from agricultural activities. Wastewater is also an important source of phosphate, which is often a constituent of detergents.

Ammonium was detected at all sampling stations in concentrations ranging between 90 - 5,468 µg/L during the wet season, and  $40 - 2,131 \,\mu\text{g/L}$  during the dry season. The TBS limit for ammonium in potable water is 500 µg/L, which was exceeded at most stations in the Msimbazi River and at some stations in the Mbezi River (Fig. 2b). The Msimbazi River was found to have the highest concentrations of  $NH_{A^{+}}$ (Fig. 2b), especially at station Ms<sub>3</sub>, whose water was detected to produce an unpleasant smell almost all along the sampling station. This was confirmed by the Friedman non-parametric test which revealed the median ranks of 211 (Kizinga River), 1,470 (Mbezi River) and 323 (Msimbazi River), ( $\chi^2(2) = 15.200$ , p =0.001). The highest concentration of 5,468  $\mu$ g/L was detected at Ms<sub>3</sub> (Fig. 2b), a station which also had lowest DO concentration. Ammonium occurs naturally in freshwaters, though in very small amounts, because of microbiological activity which causes the reduction of nitrogen-containing compounds. Usually the total ammonia concentration ( $NH_3-N$  + NH,<sup>+</sup>) in surface waters is  $<200 \ \mu g/L$  but may reach  $2,000 - 3,000 \mu g/L$ . Its contamination sources in fresh water include wastewater and fertilizers (Chapman and Kimstach 1996). The high concentrations measured at some of the Msimbazi River stations are indications of contamination, most likely from sewage and farming activities.

### Metals

The descriptive data for the measured metal concentrations from the fifteen stations are summarized in Table 4, with comparison to the Tanzanian national standards and the WHO limits.

Table 4. Ranges and mean  $\pm$  SD (N = 30) concentrations ( $\mu$ g/L) of metals in the rivers.

Metal -	Wet season		Dry s	eason	Tanzania	WHO
	Range	Mean ± SD	Range	Mean ± SD		
Al	274.2 - 938.2	$561.2 \pm 223.2$	241.5 - 746.0	$437.4 \pm 161.2$	200	200
Cr	8.0 - 43.0	$22.2\pm10.9$	1.2 - 31.6	$18.2 \pm 8.1$	50	50
Cu	0.7 - 3.2	$1.7\pm0.7$	0.3 - 3.4	$1.7\pm0.9$	1000	2000
Fe	53.1 - 119.2	$106.5 \pm 35.5$	42.6 - 112.5	$82.6\pm19.5$	300	
Pb	0.7 - 24.0	9.0 ± 7.9	0.8 - 14.6	$5.4 \pm 4.2$	10	10
Zn	114.6 – 175.6	$153.3 \pm 13.9$	44.6 - 125.7	$84.4\pm23.3$	500	300
Cd	BDL	-	BDL	-	3	3

BDL = Below Detection Limit

The data in Table 4 show that the Al concentration ranged between 274.2 - 938.2 µg/L during the wet season, and from 241.5 - 746.0 µg/L during the dry season. These concentrations exceed both the Tanzanian national standard and the WHO limit for Al in potable water of 200 µg/L. Aluminium occurs abundantly in nature in various concentrations depending on different physicochemical and mineralogical factors of a particular area, however it can also be easily enriched to high levels primarily due to its common use in construction, automotive, electricity, food packaging amongst other uses (WHO, 2003b). The highest concentrations during both seasons were measured at station Ms<sub>1</sub> followed by station Ms<sub>9</sub>. The Msimbazi River generally had the highest concentrations of Al compared to the other rivers during both seasons (Fig. 3). This was also confirmed by the Friedman test, which revealed statistically significant difference in Al concentrations among the three rivers as Msimbazi River (n =10, M = 666), followed by Kizinga River (n = 10, M = 458) and Mbezi River (n = 10, M = 373), ( $\chi^2(2)$ = 11.400, p = 0.003). The concentrations measured in this study, especially in the Msimbazi River, are likely to be enriched from anthropogenic sources due to the range of human activities taking place in the area.

Chromium was found to range between  $8.0 - 43.0 \mu g/L$  during the wet season and from  $1.2 - 31.6 \mu g/L$  during the dry season. These concentrations were below the Tanzanian national standard and the WHO limit of 50  $\mu g/L$ . The highest Cr concentration of 43.0  $\mu g/L$  was measured at the Msimbazi River station Ms<sub>1</sub>. The data show that generally the Msimbazi River had the highest levels of Cr during both seasons (Fig. 3). Chromium may contaminate river water through various diffuse sources arising from the use and disposal of materials and products from industrial and domestic activities.

The concentrations of Cu were  $0.7 - 3.2 \,\mu$ g/L during the wet season and  $0.3 - 3.4 \,\mu$ g/L during the dry season. These concentrations were far below the recommended Cu limit in potable water by both the TBS and the WHO limits (Table 4). The highest concentrations were again measured at the same two stations in the Msimbazi River, namely stations Ms<sub>1</sub> and Ms<sub>2</sub>, which also had the highest concentrations of Al and Cr. However, the Cu concentrations detected in water in this study are too low to raise any alarm. The concentration of Fe of 53.1 – 119.2  $\mu$ g/L during the wet season and 42.6 – 112.5 4  $\mu$ g/L during the dry season were also far below the Tanzanian national standard of 300  $\mu$ g/L. The highest concentrations during both seasons were again measured at the Msimbazi River station Ms<sub>1</sub>. The statistical test revealed that Msimbazi River had generally the highest concentrations of Fe (n = 10, M = 105.1), followed by the Mbezi River (n = 10, M = 90.2) and Kizinga River (n = 10, M = 87.3), ( $\chi^2$ (2) = 4.200, *p* = 0.022).

The concentrations of Pb were 0.7 - 24.0 µg/L during the wet season and  $0.8 - 14.6 \,\mu g/L$  during the dry season (Table 4). The maximum allowable limit of Pb in potable water by both TBS and WHO limits is 10.0  $\mu$ g/L. This limit was exceeded at six of the 15 sampling locations, including three in the Msimbazi River and three in the Kizinga River. Station Ms<sub>3</sub> had the highest Pb concentration of 24  $\mu$ g/L. Another station with a relatively high Pb concentration was Ms<sub>4</sub>, which had 16.0  $\mu$ g/L during the wet season and 14.6  $\mu$ g/L during the dry season. The Friedman test performed on Pb data from the three rivers showed that Kizinga River had generally the highest levels, followed by Msimbazi River. Low levels of Pb are expected in river waters due to natural sources such as dissolution of rocks and soils. Anthropogenic sources include the production and use of lead-containing consumer products (WHO, 2003c). Tanzania is implementing legislation restricting the use of leaded fuels (Bultynck and Reliquet, 2003), therefore its importance as one of the largest sources of lead contamination is diminishing. A high concentration of Pb such as those found in some stations in this study is considered a health risk, since Pb is toxic and has no health benefit (WHO, 2003c).

The data in Table 4 also shows that Zn was detected in concentration ranges of 114.6 – 175.6  $\mu$ g/L during the wet season and 44.6 – 125.7  $\mu$ g/L during the dry season. These concentrations are well below the WHO limit of 300  $\mu$ g/L as well as the TBS limit of 500  $\mu$ g/L. The highest Zn concentration was detected at station Ms<sub>4</sub> during the wet season. The statistical test revealed that Msimbazi River had the highest concentrations of Zn. However, the Zn concentrations observed in this study are not alarming since they were all below the recommended limits, and were within the expected ranges for rivers that vary from <10  $\mu$ g/L to >200  $\mu$ g/L (Andarani *et al.*, 2021). Cadmium was not detected within the limits of the employed method in any of the sampling stations in this study.

The metal concentrations followed the order Al > Zn >Fe > Cr > Cu > Pb > Cd. When the whole dataset consisting of the physicochemical parameters and the metal concentrations was subjected to Spearman Rank correlation analysis, it was observed that Fe was positively correlated to pH (r = 0.563, at 0.05 level, 2-tailed). Studies have found that the pH of water is important for the solubility and biological availability of Fe since its concentration increases with increasing water pH (Nagwa, 2016). Concentrations of Al, Fe and Pb were all found to positively correlate with TSS (r = 0.488, 0.467 and 0.455 respectively). This indicated that TSS played an important role on the availability of the metals in water, although other factors might have been more significant. Studies have found that suspended particles in rivers can act as carriers of potentially bioavailable metal species (Nasrabadi *et al.*, 2018). Aluminium concentrations were also found to positively correlate with turbidity (r = 0.578), probably due to the same reason.

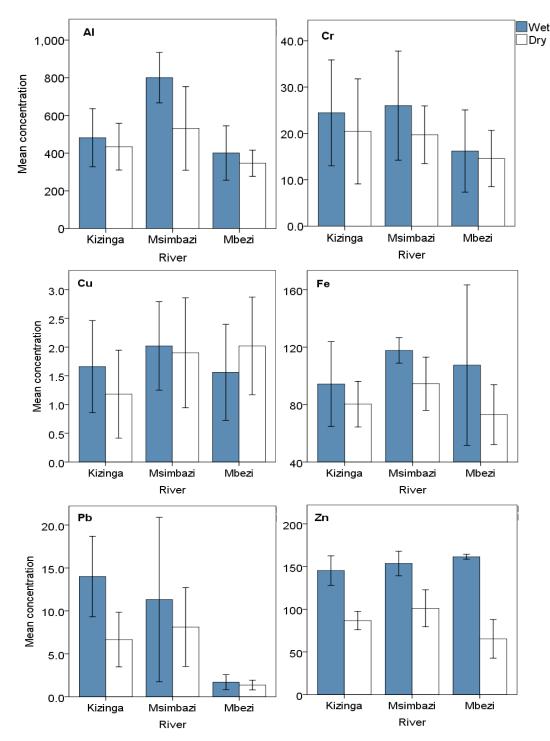


Figure 3. Mean concentrations ( $\mu g/L$ ) of the six metals in the rivers during the wet and dry seasons.

Correlation among pairs of trace metal concentrations (Table 5) showed positive correlations between Al and Fe as well as between Pb and Cr. This indicated that the pairs were probably from the same sources.

### Seasonal variations

On analyzing the seasonal variations of pH values by the Wilcoxon signed-ranks test, a statistically significant difference was observed, with higher values recorded during the wet season (n = 15, M = 8.28, SD =1.08) than during the dry season (n = 15, M = 7.91, SD = 0.53), (z = -1.108, p = 0.021). This was accounted for by the fact that during the wet season rivers receive runoff that may increase water dilution and hence increase the concentrations of hydrogen ions that consequently reduce the pH. This has also been found by other researchers, e.g., Girardi et al. (2016) who studied water quality changes in rivers during rain events and found that pH showed some decreasing trends during rainfall. Statistically significant seasonal trends were also observed for both EC and TDS measurements. Higher EC values were recorded during the wet season (n = 15, M = 17,982) than the dry season (n = 15, M = 17,038), (z = -2.215, p = 0.027). Similarly, higher TDS values were observed during the wet season (n =15, M = 9,077) than the dry season (n = 15, M = 7,860), (z = -2.542, p = 0.011). These variations might be attributed to increased inputs of dissolved materials from runoff during rainfall.

The statistical test also revealed that both TSS and turbidity were significantly higher during the wet season, with respective p values of 0.007 and 0.003. This may be attributed to increased rainfall runoff from the land that carries different sorts of materials into the rivers. Another contributing factor may be increased erosion of bottom material due to higher discharges. The same trend was also observed by other researchers such as Anhwange *et al.* (2012), who studied the seasonal variation of water quality parameters of the Benue River, Makurdi Metropolis, Nigeria. The levels of DO were statistically significantly lower during the wet season (n = 15, M = 4.31) than during the dry season (n = 15, M = 4.85), (z = -2.160, p = 0.031). There was also a marked seasonal trend in terms of COD, where higher concentrations were measured during the wet season at all stations (n = 15, M = 724.96) than during the dry season (n = 15, M = 649.53), (z = -3.408, p = 0.001). The increase in COD during the wet season indicated higher contamination levels, probably from reception of contaminated runoff during rainfall.

The seasonal variation of alkalinity followed the same trend as those for TSS and turbidity, with which it was positively correlated. The levels were higher during the wet season (n = 15, M = 611) than during the dry season (n = 15, M = 461), (z = -2.557, p = 0.011), probably due to the same reasons. The variation in total hardness was not statistically significant between the seasons. The seasonal trend for Cl<sup>-</sup> and salinity had no statistically significant difference between the seasons for both, with p = 0.776 for Cl<sup>-</sup> and p = 0.427 for salinity.

A statistically significant difference was observed for the levels of SO<sub>4</sub><sup>2-</sup>, which were higher during the wet season (n = 15, M = 273.4) than during the dry season (n = 15, M = 254.4), (z = -3.408, p = 0.001). Similarly, concentrations of PO4<sup>3-</sup> were significantly higher during the wet season (n = 15, M = 1.31) than during the dry season (n = 15, M = 1.07), (z = -2.040, p = 0.041). The same trend was again observed in concentrations of  $NH_{4}^{+}$ , where the wet season concentration was higher (n = 15, M = 1431) than the dry season concentration (n = 15, M = 585), (z= - 3.408, p = 0.001). The increase in concentration of the three parameters during the wet season was probably due to increased inputs of contaminated run-off from human activities during rainfall. This was also observed by researchers from other locations (e.g., Anhwange et al., 2012; Tshibanda et al., 2014).

Table 5. Spearman Rank correlation matrix between pairs of metals (n = 30) in the rivers.

	AI	Cr	Cu	Fe	Pb	Zn
Al	1.000					
Cr	0.179	1.000				
Cu	0.171	0.244	1.000			
Fe	0.512**	-0.091	-0.280	1.000		
Pb	0.240	0.530**	-0.127	0.163	1.000	
Zn	0.131	0.107	-0.182	0.364*	0.130	1.000

\*. Correlation is significant at the 0.05 level (2-tailed).

\*\*. Correlation is significant at the 0.01 level (2-tailed).

Table 6. Principa	l components matrix.
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	Component							
	1	2	3	4	5			
pН	-0.022	0.273	0.859	0.175	-0.002			
TDS	0.948	-0.224	-0.044	0.096	-0.029			
EC	0.949	-0.231	-0.055	0.063	-0.055			
TSS	-0.243	0.752	0.330	0.292	0.134			
Turbidity	-0.288	0.774	0.292	0.282	0.097			
DO	0.189	-0.793	-0.366	0.183	-0.266			
COD	0.881	0.017	-0.038	-0.102	-0.123			
Alkalinity	-0.297	0.415	0.730	-0.079	0.056			
Total Hardness	0.807	-0.245	-0.143	-0.062	-0.109			
Chloride	0.955	-0.213	-0.076	0.086	-0.026			
Salinity	0.958	-0.206	-0.067	0.091	-0.018			
Sulphate	0.904	0.162	-0.146	0.074	0.012			
Phosphate	0.679	0.603	-0.109	0.032	0.031			
Ammonium	-0.072	0.844	0.004	-0.073	0.190			
Al	-0.111	0.674	0.391	0.184	-0.112			
Cr	-0.317	0.002	0.446	-0.204	0.588			
Cu	-0.079	0.187	0.371	-0.697	-0.178			
Fe	0.031	0.272	0.212	0.818	-0.205			
Pb	-0.078	0.406	-0.064	0.160	0.788			
Zn	0.126	0.194	0.324	0.502	0.322			
Eigenvalue	8.08	4.37	1.61	1.30	1.06			
% of Variance	40.39	21.85	8.06	6.60	5.32			
Cumulative %	40.39	62.24	70.30	76.90	82.22			

Extraction Method: Principal Component Analysis.

Rotation Method: Varimax with Kaiser Normalization.

Bold values = high loadings (> 0.50)

The data on concentrations of metals for the two seasons were further subjected to the Wilcoxon signed-rank test. The observed seasonal trends were such that, with the exception of Cd that was below the detection limit, and Cu which did not show any statistically significant difference between seasons, all other metal concentrations were significantly higher during the wet season than the dry season: i.e., Al (p = 0.005, z = -2.840); Cr (p = 0.049, z = -1.676); Fe (p = 027, z = -2.215, Pb (p = 0.017, z = -2.385) and Zn (p = 0.001, z = -3.408). These results showed that the metal concentrations were influenced by the weather conditions. Some possible factors that may have led to this variation include the reception of contaminated runoff from land-use practices such as agriculture and domestic and industrial activities that were conducted close to the rivers. This was also observed by researchers in locations with similar activities, e.g., Edokpayi et al., (2016) observed increased concentrations of metals during the wet

season compared to the dry season in the Mvudi River, South Africa.

### Factor reduction and Cluster Analyses

The results of factor reduction by PCA extracted five principal components with eigenvalues ranging from 8.08 to 1.06 that accounted for 82.22 % of the total variance (Table 6).

The loadings of data in the principal components matrix showed that Component 1, contributing 40.39 % of the total variance, includes high loadings from TDS, EC, COD, total hardness, chloride, salinity, sulphate, and phosphate. It showed that these eight parameters played a major role in characterizing water quality in the rivers. The high levels of these parameters suggest that this component was associated with chemical contamination of the river waters, most likely from anthropogenic sources. The high contributions of TSS, turbidity, decreased DO and NH<sub>4</sub><sup>+</sup> in

Component 2 (21.85 %) may be associated with inputs from decaying particulate materials. Component 3 (8.06 %) had loadings from pH and alkalinity, which might be associated with water chemistry such as the types of dissolved ions present in the waters. Component 4 (6.60 %) was influenced by only Fe and Zn, which showed that these metals were probably from the natural geochemical composition of the catchment, since their levels did not constitute pollution, even though they were weakly correlated. Component 5, which contributed 5.32 % of the total variance, includes high loadings from the concentrations of Cr and Pb, which suggested that the two metals were probably from the same source. Since Pb was found to be anthropogenically enriched at some locations, this was probably associated with contamination from human activities.

The results of the classification of the sampling stations into homogeneous groups using HCA based on the measured parameters are summarized in a Dendrogram in Fig. 4.

The dendrogram showed an initial splitting of the tree to form two clusters; the top cluster (Cluster 1) that contained twelve sites, and the bottom cluster (Cluster 2) that contained only three sites  $(Kz_4, Kz_5 \text{ and } Mz_5)$ . As previously observed, the three stations in the bottom cluster were characterized by

the highest levels of TDS, EC, chloride, and salinity (Figs. 3a and 3b). The initial clustering is therefore based on the four parameters. The bottom cluster is further split to group the two Kizinga River stations ( $Kz_4$  and  $Kz_5$ ) together, leaving  $Mz_5$ .

Cluster 1 is further split into two groups, the bottom one with two stations and the top one with 10 stations consisting of three Kizinga River stations ( $Kz_1$ ,  $Kz_2$ ,  $Kz_3$ ), four Msimbazi River stations ( $Ms_4$ ,  $Ms_3$ ,  $Ms_1$ ,  $Ms_2$ ), and three Mbezi River stations ( $Mz_1$ ,  $Mz_2$  and  $Mz_2$ ). The ten stations had somewhat similar trends in levels of the measured parameters. For example, the four Msimbazi River stations in this cluster had relatively high concentrations of  $NH_4^+$ , Al, Cr, Cu, Fe and Zn.

# Conclusions

The characterization of water quality in the Kizinga, Msimbazi and Mbezi Rivers along the Indian Ocean coast in Dar es Salaam, Tanzania, revealed decreased water quality in the rivers. High levels of pH, TDS, EC, turbidity, chloride, sulphate and ammonium that do not comply with the TBS and the WHO limits for potable water were detected. Furthermore, other parameters that have no specific regulatory limits, such as TSS, DO, COD, alkalinity, total hardness, salinity, and phosphate, had levels that exceed those expected for uncontaminated river waters. Concentrations of five metals (Cr, Cu, Fe, Zn and Cd) out of the seven that

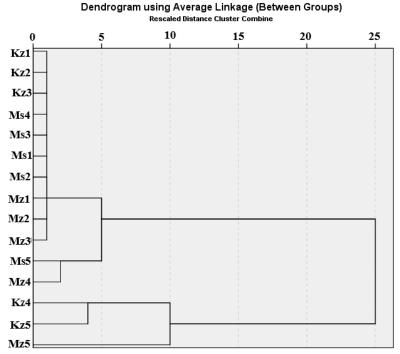


Figure 4. Dendrogram of the cluster analysis of the 15 stations.

were investigated, were found to be below the TBS and the WHO limits. Only Al and Pb were found to exceed the maximum recommended limits at some locations. The seasonal variation of the measured parameters showed that water quality was more impacted during the wet season than the dry season, with increased pH, EC, TDS, TSS, turbidity, COD, and decreased DO levels. Concentrations of  $SO_4^{2-}$ ,  $PO_4^{3-}$ ,  $NH_4^+$  and the six metals (Al, Cr, Cu, Fe, Pb, Zn) were all higher during the wet season than the dry season. Natural influences were also observed in terms of increased Cl- concentrations and salinity levels in locations closer to the ocean, due to seawater intrusion. Of the three rivers, the Msimbazi River was found to have the highest levels of Al, Cr, Cu, Pb and Zn. This is probably due to more exposure of its catchment to human activities compared to the other rivers.

Factor reduction by PCA revealed the main factors that control the observed variability to probably include chemical inputs from anthropogenic sources, decaying particulate materials, natural water chemistry in terms of types of dissolved ions present in the waters, and the geochemical composition of the catchment. These results showed that the quality of water in the three coastal rivers is not suitable for drinking and/or cooking. They also showed that the ecology of the rivers is probably impacted by human activities. These findings demonstrate that regular monitoring of the general environment and the associated land-use practices is important in this area. Strategic measures such as provision of environmental education at all levels and stipulation of clear policy statements on environmental management should therefore be adopted to ensure sustainability of these water resources.

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