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Assessing the contributions of industrial wastewater to toxic metals contamination in receiving urban rivers, Dar es Salaam City, Tanzania

Charles Kihampa[1], Gervas Kaisi[2] and Harieth Hellar-Kihampa[3,*]

[1]School of Environmental Science and Technology, Ardhi University, P. O. Box 35176, Dares Salaam, Tanzania.

[2]Tanzania Bureau of Standards, P. O. Box 9524, Dares Salaam, Tanzania.

[3]Institute of Continuing Education, The Open University of Tanzania, P. O. Box 23409, Dares Salaam, Tanzania.

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ABSTRACT

This study investigated contributions of industrial wastewater on quality of receiving urban rivers and streams in Dar es Salaam City, Tanzania, to establish their contamination levels and assess risks to human health and ecology. Water and sediment samples from 21 locations were analyzed for physicochemical parameters, nutrients and toxic metals. Pollution status was evaluated by contamination indices and comparison with benchmarks. Results showed high levels of dissolved solids, nutrients and toxic metals in water and significant levels of contamination in sediments. Poorly treated industrial effluents contributed in contaminating the receiving rivers; however significant levels of contamination were found to originate from other upstream sources as well. These findings indicate high risk to human health and the environment.

Introduction

The rapid economic expansions in most African countries have resulted into increased medium and small-scale industries which are prevalent in most cities and urban centers [1]. Majority of industrial manufacturing processes and commercial enterprises produce and discharge considerable volumes of wastewater that can contain such things as residual acids, toxic metals, organic contaminants, suspended solids, dissolved inorganic substances, oils, greases, and colouring compounds [2, 3]. The produced wastewater therefore requires adequate treatment to remove some or all of the contaminants to make it fit for reuse or discharge to the environment without endangering human health and the natural environment. However, in most of these industries, environmental management is considered as a separate part of industrial activities and is not given due considerations [4]. Studies have shown that in most cases, less than 15% of the collected wastewater is treated before being discharged [5] some of the reasons being poor operations, overloading of the available facilities, high costs of treatment facilities, lack of information, poor designs and use of outdated technologies [2, 6]

In Tanzania, the National Environmental Policy [7] and the Environmental Management Act [8] have identified environmental pollution as one of the key problems that call for urgent attention. One of the identified environmental concerns in urban areas is disposal of partially treated or untreated wastewater from domestic and industrial sources [9, 10]. This is contrary to the call for sustainable management of water and sanitation as well as inclusive, safe, resilient and sustainable cities and human settlements as addressed in the Sustainable Development Goals [11].

Dar es Salaam is the largest city in Tanzania and the most important for both business and government. It consists of three administrative districts of Kinondoni, Ilala, and Temeke, with a population of about 4.4 million [12] representing about 10% of the total population. The city is endowed with freshwater resources, including several rivers and streams. In some locations, the rivers and streams are used for different human activities including domestic supply, especially for communities living in unplanned settlements without access to regulated pipe water. Another common use is irrigation in urban vegetable farming. As a commercial centre of the country, the city also contains a significant number of medium and small-scale industries. According to the Ministry of Industry and Trade, it is estimated that more than 80% of industries that are registered in Tanzania are located in Dar es Salaam city [13]. Among the most common ones are those of food and beverage production; textile mills, garments, leather and plastic products and those of chemicals and cosmetics production. Some of these industries have connected their wastewater in the Municipal Wastewater Treatment Plants (MWTP), although most of them not designed to treat both domestic and industrial wastewaters. The underlying problem is partial treatment of the wastewaters, resulting into potential contamination of water in the receiving streams and rivers, which save as the final disposal points for the wastewater.

Previous studies that assessed pollution levels of toxic metals and other contaminants in the Dar es Salaam environment [9, 14] focusing on streams, rivers and estuaries, generally indicated that urban rivers were contaminated by toxic metals from different sources. However, there is no documented study that specifically investigated pollution levels originating from industrial effluents. This study was therefore designed to asses the contributions of industrial effluents in contaminating receiving urban rivers and streams.

Tele: +255 784443 157

E-mail address: hhellar@yahoo.co.uk, hariet.hellar@out.ac.tz

Seven industries were selected as case studies to assess the situation. First we observed and documented the wastewater handling practices in the industries, and then we sampled water and sediments from wastewater releasing points and other strategic locations of the receiving water bodies and characterized them for their physicochemical parameters and concentration levels of nutrients and some selected metal contaminants. The objectives were to determine contributions of the industrial effluents in contaminating the receiving waters, to quantify levels of the resulting contamination and to assess the suitability of the receiving urban rivers and streams for human activities.

Materials and Methods

Description of the study area and sampling locations

Dar es Salaam city is located at 6°48' South and 39°17' East along the Indian Ocean coast. The total surface area of the city is 1,800 Km^2, comprising of 1,393 Km^2 of land mass. Due to its close proximity to the equator and the Indian Ocean, the city experiences tropical climatic conditions characterized by hot and humid weather throughout much of the year. The average low temperature ranges from 22 to 25 °C and the average high temperature is between 30 and 36°C. The city has two rainy seasons; "the long rains" in April and May and "the short rains" in November and December, the annual precipitation is estimated at 1,100 mm in a normal year.

Seven industrial locations were pre-selected for this study to investigate inputs from identified industries that were observed to be discharging effluents to the urban rivers and streams. The industries' names, locations and the respective rivers and streams into which their effluents are discharged are summarized in Table 1, while Figure 1 is the map of Dar es Salaam city showing locations of the industries and the sampling points.

The Tanzania Breweries Limited (TBL) and the Serengeti Breweries Limited (SBL) deal with production of malt beer, non-alcoholic malt beverages and alcoholic fruit beverages. Both TBL and SBL have state-of-art wastewater facilities that apart from treating the wastewater, they also save as sources of energy through production of biogas (Company Manuals). TBL disposes its wastewater in the Msimbazi River, while SBL disposes in the Kibasila stream. The Nida Textile Mills located along the Nelson Mandela Highway and the Tanzania Tooku Garments Company Limited located at the Export Processing Zones Authority (EPZA) deal with textile production. Both have on-site Effluent Treatment Plants (ETP) where wastewater is allowed to settle for some time before being pumped into Ubungo River and Kimanga River, along the Morogoro Road deals with textile processing that normally produces large volumes of wastewater from different processes, often rich in dyestuffs, inorganic and organic chemicals, detergents, soaps and finishing chemicals [15, 16].

The industry conducts *in-situ* coagulation-flocculation treatment to eliminate organic substances and later dispose its wastewater in the Municipal Wastewater Treatment (MWT) facility. Effluent from the MWT is then released into Luhanga stream, which then pours its water into the Msimbazi River. The Murzah Ltd. and the Royal Ltd. both located along the Nelson Mandela highway in Kinondoni District produce soaps and detergents. The industries have coagulation-flocculation treatment method in which they apply aluminum sulfate coagulant and later disposed their wastewater effluents into Msimbazi and Ubungo Rivers, respectively.

For each industry, samples were collected from three points as indicated in Table 1; upstream of the receiving body before confluence with industrial effluents; the discharged effluents at the point of release to the receiving body and downstream the receiving body after confluence with the industrial effluent. Figure 2 illustrates positions of the three sampling points in relation to the industries and the water flow of the receiving bodies. Different human activities are carried out upstream and downstream of the rivers and streams, including irrigation for green vegetable farms, fishing, cars and cloths washing and extraction of sand for construction activities. Figure 3 shows the general environment of some of the investigated sites.

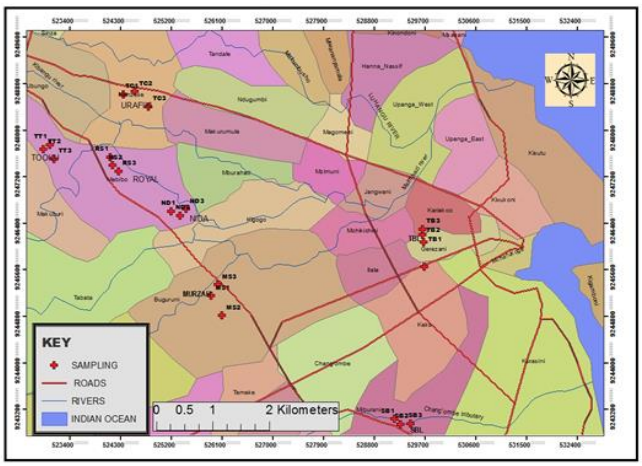

Figure 1. Map of Dar es Salaam City showing sampling locations for this study

Table 1. Sampling points in the vicinity of seven industries in this study

Sampling site	Geographical Position	River/Stream	Sample Code		
			Upstream	Wastewater	Downstream
Tanzania Breweries Ltd.	E0529661 N9246211	Msimbazi	TB1	TB2	TB3
Serengeti Breweries Ltd.	E0529268 N9242953	Kibasila	SB1	SB2	SB3
NIDA Textile Co. Ltd.	E0525334 N9246578	Ubungo	ND1	ND2	ND3
Tanzania Tooku Garments Ltd.	E0523083 N9247653	Kimanga	TT1	TT2	TT3
Tanzania-China Friendship Textile Ltd.	E0524525 N9248715	Luhanga	TC1	TC2	TC3
Murzah Soap & Detergents Ltd.	E0526080 N9244964	Msimbazi	MS1	MS2	MS3
Royal Soap & Detergents Ltd.	E0524142 N9247485	Ubungo	RS1	RS2	RS3

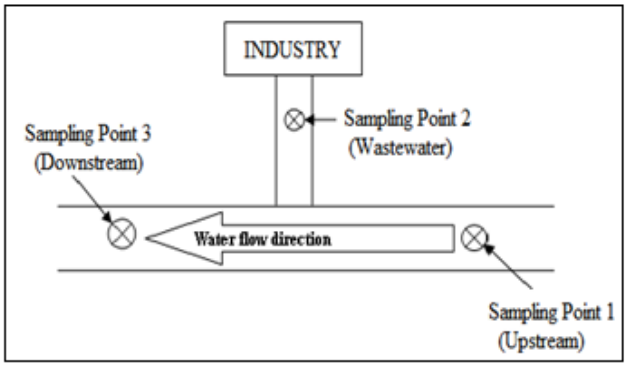

Figure 2. Schematic of locations of the sampling points with respective to the industries

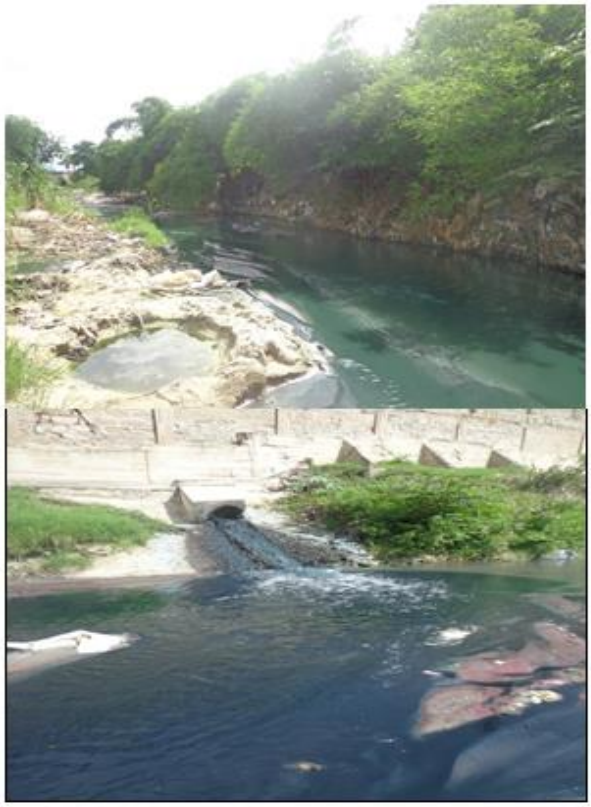

Figure 3.General environments of some of the sampling locations in this study

A total of 42 samples comprising of 21 water samples and 21 sediment samples were collected during the rainy season in April 2015. Water samples were collected using 500 mL plastic bottles that were pre-soaked overnight with 10% HCl, rinsed with distilled water and later rinsed with effluent/stream water before sample collection. Preservation of water samples was done by adding 2 drops of concentrated HNO_3.Sampleswere stored below 4°C for some hours until analysis. The physicochemical water quality parameters Total Dissolved Solids (TDS), Electrical conductivity (EC), Salinity, temperature and pH, were measured on site using hand-held portable monitors. TDS, EC and salinity were measured using a portable HACH®sensION 156 Conductometer, while temperature and pH were measured using portable HANNA® meter with pH and temperature probes. Both the pH and conductivity meters were calibrated using the manufactures' -provided solutions before measurements. About three measurements were taken for each parameter at each sampling station and the mean values for each sampling location were calculated.

Sediment samples were collected at a depth of 0 – 5 cm using a stainless steel scoop following standard protocols [17]. Approximately 200 g sample was collected at each sampling point, wrapped in aluminum foil and stored into polypropylene air tight bags. Both water and sediment samples were kept in cool boxes and transported to the Laboratory of the School of Environmental Science and Technology, Ardhi University in Dar es Salaam for further processing.

Sediments were characterized for their organic matter content using the Sequential Loss on Ignition methods described in the Methods Manual for Characterization of Sediments [18]. Sample crucibles were pre-dried at 105^{o}C overnight in an oven, and then sediment sub-samples of approximately 5g were placed in the crucibles and heated in a muffle furnace to a constant mass at a temperature of 550±25^{o}C. The ignition process took about 2 h, after which the samples were allowed to cool to a room temperature. The difference in mass before and after the ignition process was used to calculate the loss in ignition and expressed as a percentage of the original weight.

Sample analysis

Determination of metal contaminants in both water and sediment samples was done by using a Perkin Elmer Analyst 100 Atomic Absorption Spectrophotometer (AAS) with Perkin Elmer HGA 850 Graphite Furnace and Perkin Elmer AS 800 Auto-sampler, made in Germany and available at the laboratory of the School of Environmental Science and Technology, Ardhi University. Water samples were analyzed directly without any pre-treatment. Sediment samples were oven dried at 105^{o}C for 24h, followed by grinding and sieving using a 0.18 mm sieve. A dry sediment sub-sample of 0.5 g was placed into a graduated test tube and mixed with 2 mL of *aqua regia* 1:3 (1 part HCl: 3 parts HNO_3). The mixture was digested on a hot plate at 95^{o}C for 1 h and allowed to cool to a room temperature. The sample was then diluted to 10 mL using distilled water and left to settle overnight. The supernatant was filtered prior to determination of metals by AAS.

Nutrients concentrations were determined by the method described by [19]. For phosphate determination, water samples previous filtered and preserved with H_2SO_4 were treated with phos ver®3 phosphate pillow in 25 ml of water sample, followed by vigorous shaking to obtain a uniform mixture which was allowed to settle for 5 min for the reaction to take place. A DR-5000 spectrophotometer was set and run at a wavelength of 890 nm. Instrumental blanks were used for calibration and quality check. The same procedure was done for nitrate determination, using nitra ver®5 nitrate reagent at a wavelength of 890 nm.

The quality of the analytical procedure was assuredly analysis of standard reagents and procedural blanks. During the analytical process, standard were run after every five sample readings to ensure that margin of error is within 5%. In every analytical batch, 10% of all samples were analyzed repeatedly to ensure the precision and accuracy of analysis. A 10 cm long slot-burner head, a lamp and a standard air acetylene flame were used. The AAS detection limit was 0.01 ppm (0.01 mg/Kg), slit width 0.07 mm and elements wavelength were 213.9, 283.3, 228.8, 324.8 and 357.9 nm for Zn, Pb, Cd, Cu and Cr, respectively.

Data analysis

For interpretation of the results the data set were analyzed by descriptive statistics (range, mean and standard deviations) using scientific statistics software published by GraphPadInstat 3 Inc, California-USA and Microsoft Excel. Non-parametric test for multiple related samples was employed to compare concentrations of individual elements among groups of sampling locations, using the statistical package SPSS Statistics 17.0. Considered significant differences were those with $p \geq 0.05$.

Results and Discussion

Physicochemical water quality parameters

The results of pH, temperature, TDS, EC and salinity measured in water samples from the 21 locations investigated in this study are summarized in Table 2, showing levels of the parameters measured at the upstream locations, at the confluence of the industrial effluents and the river water and at the downstream locations.

Data in Table 2 show that the values of pH ranged from slightly acidic (6.75±0.21) to alkalinic (12.08 ± 0.03). The WHO set a maximum permissible pH limit of 6.5 – 9.2 for potable water [20**]** while the Tanzania standards for municipal and industrial wastewater intended for disposal into surface water is pH 6.5 – 8.5 [21**]**. These limits were exceeded in several locations. The highest pH value was measured at RS2, which is the effluent discharge point at the Royal soap and detergents industry into the Ubungo River. High pH level at this point is attributed to chemicals used in soap making processes which are alkaline in nature, such as sodium bicarbonate and sodium hydroxide. The upstream point of Ubungo River before discharge of effluents from this industry (RS1) had an average pH of 7.31 ± 0.05 while the downstream point of the same river (RS3) had a pH of 9.27 ± 0.02. This indicates the contribution of effluents from the soap industry in altering the pH of the natural river. Similarly, effluent from the other soap and detergent industry (Murzah) was alkaline and significantly increased the pH value of the Msimbazi River at the downstream point. The pH values of effluents within the allowable WHO limit [20] and the Tanzania standards [22], and did not significantly alter the pH of the river waters into which they were discharged. The lowest pH value was measured in effluents from the Tanzania Tooku Garments (TT2).

Water temperature ranged from 29.33 ± 0.50, recorded upstream the Msimbazi River (TB1), to 36.17 ± 0.06 recorded in effluents from the NIDA Textile industry (ND2). Except for the ND2 location, the recorded temperatures were within the Tanzania standard of 20 – 35 ^{o}C [21] and mostly reflected the climatic condition of Dar es Salaam city. The ND industry has a small pond where wastewater from the processing section is retained for some time to allow it to settle and cool before being pumped into the Ubungo River. However, during the sampling campaign for this study, it was observed that the industry did not observe proper retention time because effluents were released with temperatures higher than 35^{o}C, thus raising the temperature of the receiving waters. This is proved by the fact that the upstream point at the Ubungo River just before confluence with the industrial discharge (ND1) had lower temperature (34^{o}C.) The increased water temperature in the receiving river is therefore due to water being released from processing lines without being retained for sufficient time to allow it to cool. This is thermal pollution, which can destroy aquatic life in the river system. Studies have indicated that changes in water temperature by even a few degrees could indicate a source of unnatural warming of the water [23].

Total Dissolved Solids (TDS) is a measure of the total amount of all natural and anthropogenic materials dissolved in the water or the mass of residue remaining when a measured volume of filtered water is evaporated. In this study, TDS was recorded in a range of 450 to 3,210 mg L^{-1}.The highest value was recorded at the effluent of the Murzah Soap and Detergent Industry (MS2) where the industry discharges its effluents into the Msimbazi River.

Table 2. Physico-chemical properties and nutrients concentration in water samples

Site	pH	Temp (^{o}C)	TDS (mg/L)	EC (µS/cm)	Salinity(ppt)	NO_3^-N (mg L^{-1})	PO_4^{2-}–P(mgL^{-1})
TB1	7.47±0.31	29.33±0.50	1620	2597	0.73±0.06	15.17 ± 0.92	22.91 ± 0.11
TB2	7.30±0.20	32.17±0.31	2740	2980	1.47±0.04	7.07 ± 0.89	17.10 ± 0.20
TB3	7.37±0.21	32.60±0.36	1690	1665	0.87±0.06	3.24 ± 0.92	11.53 ± 0.35
SB1	7.57±0.06	30.37±0.06	1330	1069	0.47±0.05	16.21 ± 0.92	25.14 ± 0.23
SB2	7.57±0.06	33.50±0.10	3160	2839	1.47±0.06	6.19 ± 1.17	20.74 ± 0.38
SB3	7.21±0.02	33.57±0.06	1160	1764	0.87±0.07	2.50 ± 0.51	19.64 ± 0.40
ND1	7.90±0.02	34.57±0.07	1040	3229	1.70±0.10	2.50 ± 0.67	21.33 ± 0.35
ND2	11.66±0.03	36.17±0.06	2780	5620	2.97±0.06	2.80 ± 0.68	3.87 ± 0.25
ND3	11.12±0.02	35.83±0.08	1210	3969	2.07±0.06	1.92 ± 0.26	6.67 ± 0.33
TT1	7.94±0.02	33.23±0.06	1330	910	0.40±0.12	6.19 ± 0.89	0.37 ± 0.23
TT2	6.75±0.21	29.67±0.05	1060	4480	2.33±0.12	2.65 ± 0.44	3.78 ± 0.16
TT3	6.83±0.03	29.91±0.01	1410	4359	2.03±0.06	1.92 ± 0.28	7.36 ± 0.36
RS1	7.31±0.05	34.20±0.02	1440	2660	1.33±0.06	2.03 ± 0.46	23.88 ± 0.11
RS2	12.08±0.03	30.50±0.02	990	17609	10.37±0.06	14.29 ± 1.11	2.56 ± 0.29
RS3	9.27±0.02	32.09±0.01	590	3050	1.57±0.06	1.93 ± 0.17	15.10 ± 0.14
TC1	6.82±0.02	32.03±0.03	450	1147	0.50±0.11	2.26 ± 0.26	7.09 ± 0.19
TC2	11.96±0.03	33.79±0.01	2250	9309	5.20±0.09	2.43 ± 0.28	0.54 ± 0.25
TC3	6.95±0.04	31.60±0.03	960	1170	0.60±0.03	1.92 ± 0.18	8.13 ± 0.28
MS1	9.29±0.02	31.20±0.02	1710	2740	1.37±0.06	58.20 ± 0.92	8.15 ± 0.23
MS2	10.35±0.02	30.58±0.03	3210	5101	2.73±0.06	6.04 ± 1.55	7.53 ± 0.17
MS3	9.02±0.02	31.88±0.03	920	2560	1.37±0.06	7.35 ± 0.69	2.22 ± 0.15

The WHO acceptable TDS level for water intended for human consumption is 1000 mg L^{-1} [20], while the US EPA recommends maximum TDS level of 500 mg L^{-1} [17]. Most of the industrial effluents had high levels of TDS exceeding the recommended limits, for example 3160 mg L^{-1}, 2780 mg L^{-1}, 2740mg L^{-1} and 2250mg L^{-1} were measured at SB2, ND2, TB2 and TC2, respectively. This indicates the presence of ionic compositions from chemicals used in different manufacturing processes that were loaded in the effluents. High level of TDS is an indication of potential presence of contaminants such as toxic metals and dissolved ions in the water.

Data in Table 2 also show that mean concentrations of EC in the water samples varied from 910 ± 2 to 17,609 ± 2 µS/cm. The highest conductivity was measured in effluent from the Royal Soap & Detergents Company (RS2) at the discharge point to the Ubungo River. Electrical conductivity which is a measure of the ability of water sample to convey an electric current varies directly with TDS [24] as it was also observed in this study. The lowest EC reading was recorded at the upstream point of Tooku garment (TT1) at the Kibangu stream before mixing with effluent from the textile industry. This is evidence that the garment industry alters the natural quality of the Kibangu stream.

Levels of salinity in water samples measured in this study ranged from 0.40 ± 0.06 to 10.37 ± 0.06 ppt. Similar to EC values, the highest salinity level was also recorded at RS2. Salinity is a measure of dissolved mineral salts such as calcium, magnesium, potassium, sodium, sulfate and chloride, and is an important factor in determining many aspects of the chemistry of natural waters. Natural water has a salinity of up to 0.5 ppt; however anthropogenic inputs such as industrial activities may add more salt to the water thus increasing its salinity. High salinity levels measured in industrial effluents at several locations in this study (e.g. TC2, ND2, TT2 and MS2) indicate inputs of salts from anthropogenic activities as was observed in similar studies [25].

Nutrients levels in water

The data in Table 2 show that the mean concentrations of NO_3^-–N ranged between 1.92 ± 0.18 mg L^{-1} and 58.20 ± 0.92 mg L^{-1}. The highest level was recorded at MS1 at upstream the Msimbazi River before discharge of effluents from any of the industries. Concentrations of NO_3^-–N in effluents discharged at the Msimbazi River at other locations (TB2 and MS2) were only 7.07 ± 0.89 and 6.04 ± 1.55 mg L^{-1}, indicating that nutrient enrichment at upstream Msimbazi River is from different sources other than the industrial effluents. WHO maximum permissible limit of NO_3^--N in portable water is 10 mg L^{-1} (WHO 2004). In this study, apart from MS1, other locations that exceeded the WHO limit were SB1 (16.21 ± 0.92 mg L^{-1}), TB1 (15.17 ± 0.92 mg L^{-1}) and RS2 (14.29 ± 1.11 mg L^{-1}). Among the sources of nitrate in water are nitrogenous fertilizers. It was observed during the course of this study that green vegetable farming is common in various locations of Msimbazi River and therefore could contribute to nutrient enrichment.

Levels of phosphorous measured in this study ranged from 0.37 ± 0.23 to 25.14 ± 0.23 mg L^{-1}. The maximum level of phosphorous allowed by the Tanzania Standard for Municipal and Industrial wastewaters [21] is 6 mg L^{-1}. The lowest level was measured upstream Kimanga River (TT) and the highest level was measured upstream Kibasila River (SB1). Both the effluent (SB2) and the downstream location (SB3) had significantly high levels of phosphorous. Other locations that recorded high levels of phosphorous were RS1 (23.88 ± 0.11 mg L^{-1}), TB1 (22.91 ± 0.11 mg L^{-1}) and ND1 (21.33 ± 0.35 mg L^{-1}), all of them upstream locations before confluence with the industrial effluents. This indicates that phosphorous inputs were from other sources other than the industrial effluents. Possible sources of phosphates in these locations include agricultural fertilizers and detergents from human activities along the river banks. High levels of plant nutrients such as those recorded in this study are major environmental stressors in the receiving water bodies and can cause eutrophication and hypoxia [26].

Table 3. Mean concentration of metal contaminants in water samples (mg L^{-1})

Sample	Mean concentration± SD, n=3, CL=95%				
	Pb	**Zn**	**Cd**	**Cu**	**Cr**
TB1	Bdl	0.03±0.01	Bdl	Bdl	0.05±0.01
TB2	Bdl	0.07±0.05	Bdl	Bdl	0.16±0.01
TB3	Bdl	0.04±0.01	Bdl	Bdl	0.60±0.11
SB1	Bdl	0.02±0.01	Bdl	Bdl	0.02±0.01
SB2	Bdl	0.06±0.01	Bdl	Bdl	0.14±0.01
SB3	Bdl	0.05±0.01	Bdl	Bdl	0.28±0.01
ND1	Bdl	Bdl	Bdl	Bdl	0.15±0.03
ND2	Bdl	Bdl	Bdl	0.07±0.01	Bdl
ND3	Bdl	Bdl	0.01±0.01	0.02±0.01	0.07±0.01
TT1	0.26±0.01	Bdl	Bdl	Bdl	0.22±0.01
TT2	0.18±0.01	Bdl	0.06±0.01	Bdl	0.03±0.01
TT3	0.17±0.01	0.02±0.01	Bdl	Bdl	0.18±0.11
RS1	0.22±0.01	0.02±0.01	Bdl	0.02±0.01	0.15±0.01
RS2	0.56±0.01	0.15±0.01	0.02±0.01	0.16±0.01	0.67±0.01
RS3	0.26±0.01	0.20±0.26	Bdl	Bdl	0.16±0.01
TC1	0.12±0.01	0.09±0.01	0.02±0.01	Bdl	0.08±0.01
TC2	Bdl	0.05±0.01	0.02±0.01	0.04±0.01	Bdl
TC3	0.02±0.01	0.08±0.01	0.02±0.01	Bdl	0.04±0.01
MS1	0.13±0.01	0.07±0.01	0.02±0.01	0.02±0.01	Bdl
MS2	0.18±0.01	0.22±0.01	0.06±0.01	0.07±0.01	0.53±0.02
MS3	0.16±0.01	0.05±0.01	0.07±0.01	Bdl	0.08±0.01
TZS	**0.1**	**5**	**0.1**	**2.0**	**1.0**

Bdl = Below detection limit

Concentrations of metal contaminants in water

Table 3 presents mean concentrations of the six investigated metal contaminants (Pb, Zn, Cd, Cu and Cr) in water samples, providing the Tanzanian standard (TZS, 2006) of the respective metals for comparison. The data in Table 3 show that mean concentrations of Pb ranged from 0.02 ± 0.01to 0.56±0.01 mg L^{-1}. Water samples from TT, RS and MS had levels exceeding the Tanzanian limit, while samples from TB, SB, and ND were free of Pb as per the method detection limit. The highest concentration of Pb was measured in effluents from the Royal Soap and Detergent Industry (RS) at the discharge point to the Ubungo River, indicating its contribution in contaminating the river. Soap and detergent manufacturing consists of a broad range of processing and packaging operations, from which different kinds of contaminants may be released. However, the Pb concentrations measured at the upstream locations that ranged from 0.13 to 0.26 mg L^{-1} indicate contributions from other upstream locations. Lead (Pb) is purely toxic to human and micro-organisms and has no positive role even at trace concentrations in the human body; instead it has a cumulative effect and can be stored in different body parts [27].

Other toxic metals that were measured in water samples in this study i.e. Zn (Bdl – 0.22 ± 0.01); Cd (Bdl – 0.07 ± 0.01); Cu (Bdl – 0.16 ± 0.01) and Cr (Bdl – 0.67 ± 0.01) were all below the recommended limits as per the Tanzania standard (TZS, 2006). However, the mere presence of these contaminants in the water samples is an alarming sign to human health and the environmental. The presence of heavy metals in wastewater has serious impacts to surface and groundwater. For example, contamination of water with Cu may lead to copper toxicity, which is a fundamental cause of Wilson's disease [28]. Studies have also revealed that exposure to low levels of Cd may cause adverse health effects in the form of kidney damage, bone effects and fracture [29]. Long term exposure to Cd may lead to renal dysfunction while high exposure levels could cause obstructive lung disease, cadmium pneumonitis, osteromalacia, osteoporosis, increased blood pressure and myocardic dysfunctions [30]. Zinc is one of the essential trace elements that play an important role in physiological and metabolic processes of many organisms. Due to its restricted mobility, it is a metal which shows fairly low concentration in surface water. However, high concentrations of Zn can lead to system dysfunctions, which may result in growth and reproduction impairment. The clinical signs include diarrhea, vomiting, icterus (yellow mucus membrane), bloody urine, anemia, kidney failure and liver failure [30].

Organic matter content and concentrations of metal contaminants in sediments

The levels of organic matter (OM) contents measured in sediment samples from the 21 sites are summarized in Figure 4.

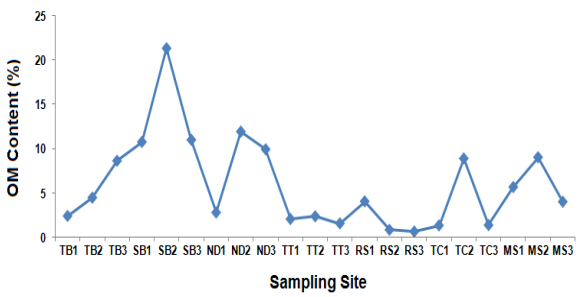

Figure 4. Organic matter content in sediments

The data reveal a percentage range of 0.67 to 21.35% with the highest value measured in sediments fromSB2 and the lowest at RS3. Organic matter content is an important factor in controlling the distribution of trace metals in sediments [31]. The relative high content of organic matter measured at these locations means that heavy metals are likely to be adsorbed in large quantities in the sediments due to formation of metal-organic matter complex. Organic matter in the sediment is known to play an important role in the adsorption and retention of heavy metals as it can act as an agent to trap metals within the sediment [32].

Mean concentrations of the analyzed metal contaminants i.e. Pb, Zn, Cd, Cu and Cr in sediments from the 21 sampling locations are summarized in Figure 5, while Table 4 compares the concentration ranges to some sediment quality guidelines (SQGs). The mean concentrations of Pb ranged from 7.43± 0.27to181.12± 51.84 mg Kg^{-1}. The highest concentration was measured at SB3, which is a downstream location of the Kibasila stream from the Serengeti Breweries Industry (Table 1), followed by SB1 (139.0 mg Kg^{-1}). Among the 21 sampling stations, eleven of them had Pb concentrations exceeding the SQG (Table 4). Station SB had generally the highest level of Pb, while TB had the lowest level. In assessing the contributions of industrial effluents to Pb contamination in the receiving waters, two different trends were noted. In one group, concentration levels recorded at the confluence points from the industries were lower than those recorded at the upstream locations. This was observed at SB where the upstream location (SB1) had 139.0 mg Kg^{-1}while the wastewater discharge point (SB2) had 39.54 mg $Kg^{-1}$and the downstream location (SB3) had 181.12 mg Kg^{-1}. The same trend was observed at TB, TT and RS. This trend indicates that the rivers and streams were already contaminated by Pb at the upstream locations before mixing with the industrial effluents; and that industrial effluents were also contaminated by Pb, which increased the Pb concentrations in receiving waters to make even higher Pb levels in the downstream locations. Other Pb sources in upstream locations may include urban run-offs especially in areas close to highways from the use of leaded gasoline [33]. A different contamination trend was observed in locations ND, TC and MS where the effluents discharge points had higher concentrations than their respective upstream and downstream locations, indicating their positive contribution in contaminating the receiving waters.

The concentrations of Zn found in the sediment samples ranged from 31.5 to 277.7mg Kg^{-1}. The highest concentration was measured at SB followed by MS (257.5 ± 0.3 mg Kg^{-1}). In five of the locations, Zn concentrations exceeded the SQG. Regarding the contamination trends, it was observed that in five of the stations (TB, ND, TT, RS and TC), the concentrations of Zn were higher at the upstream locations than the wastewater locations. For example, the Zn concentration at TB1 was 193.3 mg Kg^{-1}while at TB2 it was only 31.5 mg Kg^{-1}, similar to what was observed for the Pb profile. Sediment samples were therefore contaminated by Zn from the industrial wastewaters as well as from other upstream sources. The major sources of Zn in industrial wastewater include galvanized metal surfaces, motor oil and hydraulic fluids and tire dust [34].

The mean concentration of Cd ranged from 0.77 ± 0.17 to 5.45 ± 0.19mg Kg^{-1}. Eighteen of the 21 stations had concentrations exceeding the SQG limit of 0.99 mg Kg^{-1}. The highest concentration was measured atND1, upstream the

Ubungo river before confluence with the industrial effluents. This indicates that the major part of Cd contamination is from upstream sources. Cadmium is widely dispersed in the environment through different man-made sources such as usage of fertilizers, sewage and sludge and various industrial sources such as metal smelters, batteries, pigments and plastics [35].

Mean concentration of Cu ranged from 3.8 ± 0.3 to 128.9 ± 1.4 mg Kg^{-1}. The SQG limit of Cu in sediments is 31.6 mg Kg^{-1}. Eight of the sampling locations had Cu concentrations exceeding the SQG. The highest concentration was measured in samples collected from TT1, upstream the Kimanga river. It was also observed that concentrations of Cu were lower at the effluents points than the upstream locations before confluence with the industrial effluents in all locations. This shows that some upstream sources significantly contaminated the rivers and streams with Cu even before the discharge of the industrial effluents. Industrial releases are therefore only a fraction of Cu release in the environment in the area. Anthropogenic sources of Cu in the area may include municipal solid waste and the use of Cu containing fertilizers in agricultural activities in urban vegetable farming along the river banks.

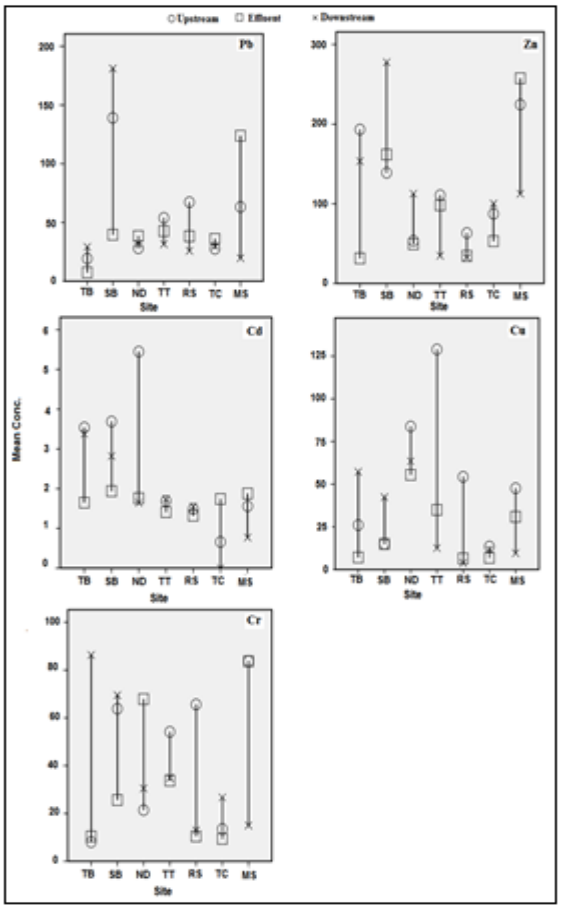

Figure 5. Mean concentration (mg kg-1, n = 3, CL = 95%) of metals in sediment samples

Chromium concentration in sediment samples from the 21 investigated stations ranged between 8.03 ± 0.35 and 86.30 ± 0.21mg Kg^{-1}. Eight of the locations had concentrations exceeding the SQG of 43.4 mg Kg^{-1}. The highest level of Cr was measured at SB3, downstream Kibasila River, followed by MS1 and MS2, which were significantly contaminated with Cr at 83.8 and 83.7 mg Kg^{-1} respectively. Effluents from all seven industries were contaminated by Cr at different concentrations.

Table 4. Comparison of metal concentration (mg kg^{-1}dw) in sediments with the acceptable limits

Metal	Mean values (this study)	Acceptable limit (SQG*)	No. of sites exceeding the SQG (n = 21)
Pb	7.43 – 181.1	35.8	11
Zn	31.5 – 277.7	121.0	7
Cd	Bdl – 5.54	0.99	18
Cu	6.50 – 128.9	31.6	8
Cr	8.03 – 86.3	43.4	8

*SQG - Sediment Quality Guidelines for Consensus Based Threshold Effects Concentration [36]

Occurrence of this metal in the industrial wastewater is supported by the fact that chromium pigments are used in leather tanning and corrosion control in some of the industries. The highest concentration of Cr in wastewater was measured at MS2 (83.7mg Kg^{-1}) followed by ND2 (67.8 mg Kg^{-1}). This indicates the significant contribution of industrial effluents to Cr contamination in the receiving waters, although other sources also contribute. Although Cr(III) is recognized as a trace element that is essential to both humans and animals, Cr(VI) compounds are recognized to be toxic and carcinogenic, and its various compounds have a wide range of potencies [37].

In order to better study the contamination patterns of metals in the three groups of sampling locations, i.e. upstream, effluents and downstream, the three sets of data for each metal were subjected to comparison using the Friedman nonparametric test for multiple related samples. The Chi-square (χ^2) and the significance level (p-value) at the degrees of freedom (df = 2) show that for the metals Pb, Zn, Cd and Cr, there were no statistically significant differences in concentration trends among the three groups of sampling locations. Concentrations of Cu were statistically different among the three groups of sampling locations, with $\chi^2(2) = 6.000$, $p = 0.050$. Further statistical analysis using the Wilcoxon signed-rank test showed that samples from upstream locations had the highest concentrations of Cu in all seven groups of locations.

Assessment of contamination levels in sediments

The degree of sediment contamination in sediment samples was further assessed by determination of contamination factors (CF) and the pollution load index (PLI). This approach evaluates the pollution load for each sampled location by expressing the concentrations of all individual metals under consideration, using the formula;

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots\ldots\ldots \times CF_n)^{1/n} \quad [38]$$

Where, n is the number of elements (5 in the present study). The CFs for each element is calculated from the relation;

$$CF = \frac{\text{Elemental concentration in the sediment sample}}{\text{Background value of the element}}$$

The world average upper earth's crust abundances for the elements Pb (20 mg kg^{-1}); Zn (79 mg kg^{-1}); Cd (0.3 mg kg^{-1}); Cu (37 mg kg^{-1}) and Cr (35 mg kg^{-1}) were used as the background concentrations for the respective metals [39]. The calculated values of CF and PLI provide useful information on pollution status and sediment quality of the investigated area and give a simplified way of comparing sediment quality between different sites. The approach has been used by a numerous authors to assess sediment contamination in different environments [e.g. 33; 34; 40].

After computation, the obtained values are compared with the established classes [38; 39]. The CF value < 1 refers to low contamination; 1 ≤ CF < 3 indicate moderate contamination; 3 ≤ CF ≤ 6 indicate considerable contamination while CF > 6 refers to very high contamination. The PLI value of less than 1 indicates that the site is unpolluted, while PLI of 1 means only baseline levels of pollutants are present and PLIgreaterthan1 indicates that the site is polluted.

Figure 6 summarizes the results of contamination factors for the five toxic metals investigated in this study, while Table 5 gives the PLI values for each site as calculated from their respective CFs. Figure 4 shows that station SB had very high contamination level of Pb, followed by wastewater at MS which was moderately contaminated by the element. The rest of the stations had mostly low levels of contamination. The CF values for Cd showed very high levels of contamination in both upstream and downstream stations TB, SB and ND and moderate contamination at most of the remaining stations. The CF values for Cd were generally the highest indicating it as a contaminant of concern among the five investigated metals in the area. The CF values for Zn, Cu and Cr varied from 0.40 to 3.50 indicating low to moderate levels of contamination.

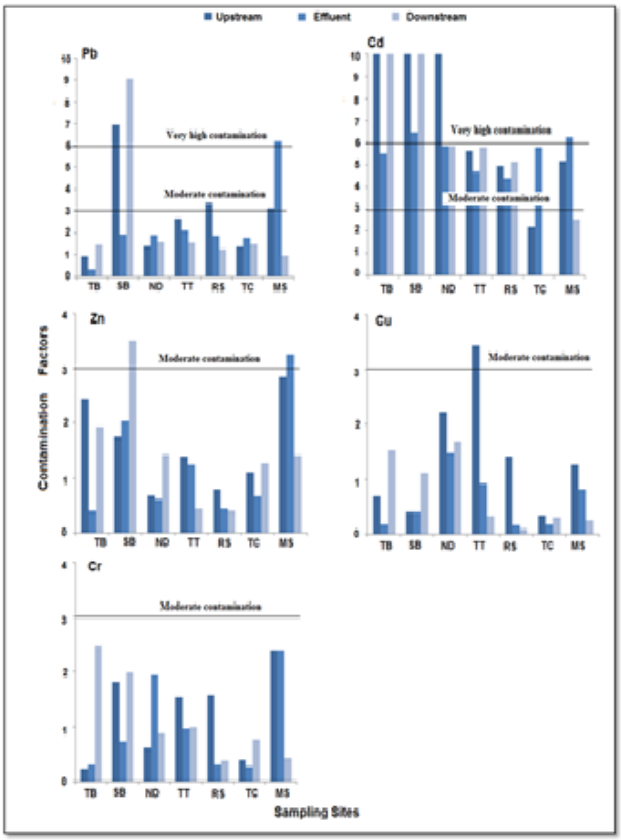

Figure 6. Contamination factors of five metals in sediment samples around the seven investigated industries

Data in Table 5 show that PLI values for the 21 locations ranged between 0.55 and 3.68. Seven of the locations had PLI values of less than 1, while 8 locations had values a little bit more than 1, and 6 locations had PLI values significantly greater than 1 (PLI = 2.56 – 3.68) indicating high level of pollution. Generally, the sampling locations around TC were the least contaminated with all three PLI values below 1, while SB was the most contaminated with all values exceeding 1. It is important to also note that sediment samples from location SB had the highest content of organic matter, especially at SB2 (Figure 4).

Table 5. Pollution Load Index values for the investigated locations

Site	PLI Values		
	Upstream	Wastewater	Downstream
TB	1.35	0.55	2.60
SB	2.56	1.50	3.68
ND	1.88	1.82	1.79
TT	2.57	1.62	1.06
RS	1.98	0.72	0.63
TC	0.86	0.80	0.85
MS	2.70	3.02	0.83

Regarding the PLI values for the effluent discharge locations, TB appears to be the least contaminated (PLI = 0.55). This is probably because the brewery industry has a modern treatment plant that combine anaerobic/aerobic treatment coupled with Reverse Osmosis (RO) which ensures reuse of the treated water in irrigation, washing and cooling purposes. The PLI value at MS was the highest for the effluent locations (PLI = 3.02) and indicated high level of contamination. The soap and detergents manufacturing industry has settling tanks where wastewater is retained for sometimes and chemicals are used to neutralize pollutants before release into the receiving waters. However, this method seems not to be efficient, and therefore water is probably released without reaching the optimal tolerance limits. For instance effluent from MS2 had a TDS value of 3,213 mg L^{-1} (Table 2) implying the presence of high level of dissolved solids.

The TC industry which had also low level of contamination in the effluent location (PLI = 0.80) treat wastewater from processing line using WSPs located at Mabibo area, about 2km from the factory, although these WSPs were constructed in the 1970s making them old and probably not so efficient. The PLI values at the TT and ND industries were also above1. These industries have installed treatment plants that involve physical and chemical processes where sedimentation, reaction and flocculation processes take place

Conclusions and Recommendations

Industrial activities have long been a source of pollutants, particularly toxic metals, into the environment. In Dar es Salaam city, the business centre of Tanzania, there have been rising concerns over pollution of urban rivers and streams from industrial sources. This study investigated the contributions of industrial wastewaters in contaminating rivers and streams by toxic metals. Analyses of water and sediment samples from the vicinity of seven selected industries in the city have confirmed that discharge of industrial effluents contribute in contaminating the receiving rivers and streams, although it was apparent that other sources also significantly contribute in the pollution. Assessment of wastewater handling practices within the industries revealed that although different types of wastewater treatment plants are utilized, some of them are not efficient, resulting into the release of poorly treated wastewater into the environment. One of the notable observations was wastewater from processing lines of a textile industry that was released without sufficient cooling, leading into raise of temperature in the receiving river.

Concentrations of the measured toxic metals exceeded the Tanzania limits and the WHO standards in a significant number of locations. Moderate to high levels of contamination by Pb, Cd, Zn, Cu and Cr were observed in almost all sediment samples.

Assessment of the pollution load using the Pollution Load Index showed high level of contamination in some of the locations. Notable case was Kibasila River downstream the Serengeti Breweries Industry (SB) which was the most contaminated site. Of the five investigated elements (Pb, Cd, Zn, Cu, Cr); element Cr significantly exceeded the SQG and had the highest contamination factor, making it of most concern. Generally, comparison of sediment concentrations with the SQG showed that the threshold effect level was exceeded in most of the locations, indicating that quality of the rivers and streams has deteriorated to the extent of making them unsuitable for human activities and a threat to aquatic life. It is recommended that appropriate legislations be enforced to make certain that industrial wastewaters are properly treated to the required standards before discharge into the environment. Regular monitoring of heavy metal pollution in the city environment is also important in order to reduce pollution problems.

Conclusions and Recommendations

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