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Pollution Potential of Effluent from Challawa Industrial Layout and its Influence on the Water Quality of River Challawa, Kano, Nigeria

Udiba U. U.*
Department of Zoology and Environmental Biology, University of Calabar, Calabar Cross River State, Nigeria

Odey M. O.
Department of Medical Biochemistry, Cross River State University of Technology, Cross River State, Nigeria

Lydia E. Udofia
Department of Biological Science, Akwa Ibom State University, ikot Akpadem, Mkpat Enin LGA, Akwa Ibom state, Nigeria

Abstract

Indicators of water quality are constituents that are measured through analysis and used to estimate the water quality status of a given sample of water. The physicochemical parameters of effluent discharged from Challawa industrial layout, Kano and its influence on the surface water quality of the receiving River Challawa, was investigated between March and June 2016 using standard analytical methods. Results indicated that both effluent and surface water showed the ranges 28.6-30.2 ^{o}C and 27.56-28.23 ^{o}C for temperature, 8.72-889 and 7.23-7.65 for pH, 3404-3844 mg/l and 2237-2499 mg/l for Total Dissolved Solids (TDS), 3667-4212 mg/l and 2435-3143 mg/l for Total Suspended Solids (TSS) and, 5602-6543 µs/cm and 1792-1954 µs/cm for Electrical Conductivity (EC). Metal concentrations of the effluents and surface water ranged from 0.86-1.49 mg/l and 0.72-1.08 for lead (Pb), 0.82-0.98 and 0.12-0.31mg/l for cadmium (Cd), 0.64-9.98 mg/l and 1.42-2.48 mg/l for chromium (Cr) and, 2.46-3.57 mg/l and 0.82-2.05 mg/l for zinc (Zn). All through the study EC, TDS, TSS, Pb, Cd, Cr, and Zn contents of effluent were found to be above the Nigerian Environmental Standards and Regulations Enforcement Agency's acceptable limit for the discharge of industrial effluents into surface water. Cd, Cr and Zn concentrations were above the Australian and New Zealand Environment and Conservation Council limits for irrigation water. The concentrations of the parameters in surface water were also found to be above World Health organization (WHO) and the Nigerian Standard for Drinking Water Quality (NSDWQ) acceptable limits for portable water. Statistical analysis revealed that effluent discharged from Challawa industrial layout has significant adverse influence on the overall water quality of River Challawa. Extraction of the effluent for irrigation purposes or surface water of the river for domestic or industrial purposes poses serious toxicological risk to human health.
Keywords: Physicochemical parameters; Water quality; Effluent; Toxicological risk; River challawa.

1. Introduction

Sometimes in the past, the three components of the environment -air, soil and water - were pure, undisturbed, uncontaminated and basically most hospitable. Today progress in science and technology is leading to environmental degradation and serious ecological imbalance which has significant adverse effects on all living organisms of the biosphere and most non living components of the global ecosystem [1]. In his adventurous expedition to satisfy his needs and aspiration for better living conditions without caring about the short term and long term changes on human and material resources arising from his actions, man exploits his environment and in so doing destroys the natural balance of the ecosystem thus creating significant environmental problems, with far reaching consequences on all the components of the environment [2]. Rapid industrialization has left with us polluted rivers, contaminated soil, depleted wildlife and exhausted natural resources. This is how the activities of mankind in his pursuit for advancement in every sphere of existence have imparted on the environment in which he lives. The by-product of these activities has led to a reduction in the quality of the land, air and water of which the environment consist. As a result, the environment of today has become foul, contaminated and harmful for the health of living organisms, including man [1]. The protection and preservation of the environment is now perceived as being of crucial importance to the future of mankind

Man whose activities pollute the environment needs to be checked in order to prevent the destruction of the environment. These human activities left unchecked could endanger the continuation of lives on planet earth. It was in response to the public perception that human health and the environment were inadequately protected that environmental laws, regulations and policies were enacted. In the bid to manage and control widespread anthropogenic environmental degradation, Nigeria formulated environmental protection policies. The first real legislation on environmental protection in Nigeria was enacted in 1988 as a wakeup call to the dumping of waste at Koko in Delta State [3]. The legislation was the Federal environmental protection agency act. Federal environmental protection agency act was the principal legislation that regulates environmental pollution in Nigeria until 2007 when The National Environmental Standards and Regulations Enforcement Agency (NESREA) act was enacted. NESREA

*Corresponding Author

remain the flagship on the regulation and enforcement of environmental laws in Nigeria. NESREA act applies to regulation, protection and development of the environment in Nigeria with the exception of the oil and gas sector. Special regulations to protect surface and ground water from pollution have been issued by NESREA. Industries have to meet concentration limits for their effluents as these are specified in facility permit issued to the industry and enforcement takes place by compliance monitoring. Ideally each industry should detoxify its effluents by the installation of pollution abatement equipments based on best practical technology (B.P.T) or best available technology (B.A.T) approach. A uniform effluent limit based on the assimilative capacity of the receiving environment(s), have been drawn up for all categories of industrial effluents in Nigeria. Additional effluent limits have been provided for individual industries with certain peculiarities [4].

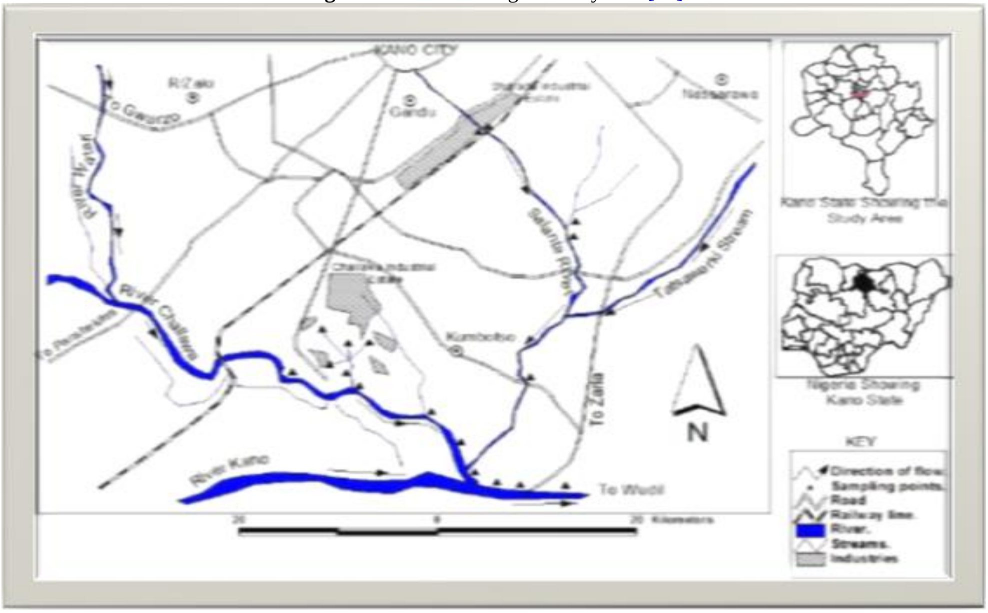
Industrial effluents are major pollutants which contaminate not only water bodies but also the entire biosphere. Tannery effluents ranked as high pollutant among all other industrial waste [5].Tanning is a chemical process that converts hides and skin to leathers, which serves as raw materials in footwear and leather industry [6]. Kano city (Latitude. 12^0 02' N, Longitude 08^0 30' E, Northern Nigeria), is significantly faced with both surface and groundwater pollution due to enormous leather and textile industrial activities [7]. Industries in the city are generally concentrated in three industrial estates, namely Bompai, Challawa and Sharada. Major industries in Challawa and Sharada industrial estates are textiles, tanneries, chemicals and allied and iron and steel Bichi and Anyata [8]. Effluent from Challawa and Sharada industries are discharged through drains and canal that empties into River Challawa. The river basin is a booming agricultural area. Crops are planted on both sides of the river bank throughout the year. The river is a major source of water supply to a number of communities located along its course. It is used for irrigation, fishing, bathing and even drinking. The river serves as intake to Tamburawa old water treatment plant, located some kilometers downstream of the effluent discharge points. NESREA and other monitoring bodies such as the Kano State Environmental Agency (KASEPA) and United Nations Industrial Development Organization (UNIDO) have made several efforts to monitor waste treatments and disposal processes in the areas. Egwuonwu, *et al.* [7] in their characterization of Topsoil and Groundwater at Challawa Industrial Area, Kano, observed that untreated and inadequately treated effluents and solid wastes produced by the tannery and textile industrial processes are indiscriminately discharged to the surrounding lands and rivers and that Farmers in the areas use the industrial waste water for the irrigation of their farm land. Levels of physicochemical parameter of River Challawa have been previously reported. However, there is need for a rational, systematic and regular assessment of the river system environment in view of the continuous discharge of effluent from the industrial areas into the river. In this study, the pollution potential of effluents discharged from Challawa industrial layout Kano and its influence on the receiving Challawa River from the point source was thoroughly assessed by determining the physicochemical parameters of water quality and heavy metals – pH, temperature, electrical conductivity, total dissolved solids, total suspended solids, lead, cadmium, chromium and zinc in effluent samples discharged from the industrial area and water samples collected from Challawa River to establish the level of compliance of industries in the area with effluent limitation standards set by the National Environmental Standards and Regulations Enforcement Agency (NESREA), and to ascertain the water quality status of the receiving Challawa River. This was done to ensure that while the developmental needs and aspirations of the present are met, the conservation and preservation of the environment for meeting future needs and aspirations are ensured. This study thus provides an independent report as against the much compromised monthly reports on the assessment of the primary effluent treatment plants submitted to NESREA by the individual industries or their consultants.

2. Materials and Methods

2.1. Study Location

Kano (Lat. 11° 59 m 18.3s N, Long 08° 32 m 05.8s E) 418 m above sea level is located in Kano State, occupies central position of Northern Nigeria [9]. Industrially, it is one of the most developed cities in Northern Nigeria with three main industrial estates namely Bompai, Challawa and Sharada. Each harbours large number of wet industries, tannery and textile are some of its dominating industries. The indiscriminate discharges of untreated effluent need to be addressed urgently. Presently the state is experiencing myrids of problems that are challenging its sustainable development [10, 11]. Effluent from Challawa industrial estate are discharged untreated or poorly treated through drains and canals that eventually flow into Chalawa River. The River (Lat 11° 52 m 41s N, Long 08° 28 m 09s E) 515 m above sea level originate from the Challawa Gorge dam in Challawa village and stretches down to River Kano where it empties into Lake Chad [9]. The river receives waste from tanneries and textile industries, urban water storm and agricultural runoff from farming communities along the river course. The river is a major source of water supply to a large number of communities along its course. It is also used for irrigation, bathing, fishing, etc. The domestic water supply for Challawa, Sharada and Bompai industrial areas and the surrounding environment in general comes from River Challawa.

Figure-1. Kano showing the study area [12]



2.2. Sample Collection and Preservation

Procedure for sample collection, preservation and preparation was adopted from APHA [13]. Three sampling points were established along the canal through which effluents from Challawa Industrial areas is channeled to River Challawa. The first point (Effluent station 1) was established at the confluence where the different drains converge. The second point (Effluent station 2) was 500 meters from Sampling station 1, the third point (Effluent station 3) was at the point just before the effluent is discharged into the River Challawa. Four sampling points were also established along Challawa River. The first point (River station 1) was at the point source (the identified effluent discharge point) and point number two (River station 2) was 500 meters downstream of sampling station 1 and the third point (River station 3) was 500 meters downstream of sampling station 2. The fourth point (River station 4) which was 1000 meters upstream of the point source (Sampling station 1) served as control. A total of seven samples were collected monthly from February to April 2016 corresponding to the peak of the dry season. Effluent and water samples were collected by simple scooping using plastic bucket and poured into 2 litres plastic containers previously cleaned by washing with detergent, rinsed with clean water, then distilled water before soaking in 10% Nitric acid for 24 hours [13]. Electrical conductivity, total dissolved solids (TDS) and temperature were determined on site electronically using HACH conductivity/TDS meter (model 44600.00, USA), pH was determined on site electronically using Zeal–tech digital pH meter (model 03112, India). The samples were kept in cooler stock with ice block and transported to the Environmental Laboratory, National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria, at a temperature of < 4^oC for preparation and analysis.

2.3. Sample Preparation and Analysis

Total suspended solid was determined according to Ademoroti [14]. A glass fibre filters paper 5.5mm diameter was dried to a constant weight in an oven at 105^0C. It was then cooled to room temperature in a desiccators and the weight noted. A gooch funnel about the same size of the glass fibre was prepared. Rubber adapter and a filtering flask were fixed and connected to vacuum pump. The glass fibre was carefully placed in the funnel. A 100ml of a well shaken sample was quickly filtered. The glass fibre was carefully removed, dried to a constant weight at 105^0C and suspended solid calculated accordingly.

The samples for metal determination were digested according to Standard Methods for the Examination of Water and Waste Water, American public Health Association [13]. Each sample was thoroughly mixed, 20ml was transferred into a conical flask, 10ml concentrated nitric acid was added and brought to slow boiling before evaporating on a hot plate to lowest volume (about 5 ml). Concentrated nitric acid was added as necessary until digestion was completed as indicated by light colour or clear solution. The digest was filtered into 50 ml volumetric flask and made up to the mark with distilled deionized water.

2.4. Metal Analysis

Lead (Pb), Cadmium (Cd), Chromium (Cr) and Zinc (Zn) concentrations in the digests were determined by Atomic Absorption Spectrophotometry, using Shimadzu Atomic Absorption Spectrophotometer (model AA-6800, Japan) equipped with Zeaman background correction and graphite furnace at National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria. The calibration curve was prepared by running different concentrations of the standard solutions. The instrument was then set to zero by running the respective reagent blanks and metal concentrations determined. Average values of three replicates were taken for each determination.

2.5. Analytical Quality Assurance

In order to check the reliability of the analytical method employed for metal determination, one blank and combine standards was run with every batch of samples to detect background contamination and monitor consistency between batches. The result of the analysis was validated by digesting and analyzing Standard Reference Material coded IAEA-336 following the same procedure. The analyzed values and the certified reference values of the elements determined were compared to ascertain the reliability of the analytical method employed. All the reagents used- HNO_3 (Riedel-deHaen, Germany), H_2SO_4, (Sigma Aldrich, Germany) and $HClO_4$ (British Drug House Chemicals Limited, England) were all of analytical grade.

2.6. Statistical Analysis

Data collected was subjected to statistical test of significance using the Analysis of Variance (ANOVA) test to assess significant variation in concentrations of physicochemical parameters and metal levels across the sampling locations. Probabilities less than 0.05 ($p < 0.05$) was considered to be statistically significant. Duncan multiple test/Donnette T was adopted for multiple comparison of parameters between sampling stations depending on whether the homogeneity test was greater than or less than 0.05. Pearson product moment correlation coefficient was used to determine the association between parameters at $\alpha = 0.05$. SPSS software 17.00 for windows was used for all statistical analysis.

3. Results

To evaluate the accuracy and precision of the analytical procedure employed standard reference materials coded IAEA - 336 was analyzed in like manner to the samples. The analyzed values were found to be within the range of the certified reference values for the metals determined (Table 1) suggesting the reliability of the method employed.

Table-1. Results of analysis of reference material (IAEA -336) compared to the certified reference value (mg/kg).

Element (mg/kg)	Pb	Cr	Cd	Zn
A Value	5.25	0.140	4.00	55.78
R value	4.2-5.5	0.1-2.34	3.1- 4.1	56-70

A Value = Analyzed value *R Value = Reference value*

Result obtained from the determination of physicochemical characteristics of both industrial effluents discharged from challawa industrial layout and surface water across the different sampling points along Challawa River, Kano around Challawa Industrial Area are presented in Table 2 while the spatial distribution of the average concentration of physicochemical properties of surface water across the different sampling points in the study area and the controls are shown in Figures 2 to 4.

Table 2 indicates that the order of detection of pH of industrial effluent was; Effluent Station 1 > Effluent Station 2 > Effluent Station 3. Effluent pH values ranged between 8.72 and 8.89. The lowest pH value (8.72) was recorded at Effluent Station 3 in the month of April and the highest (8.89) at Effluent Station 1 in March. The Effluent pH values were found to decrease gradually from the point of entry into the canal and were lowest at the point of discharge into the River. Statistical analysis shows that the difference in effluent pH across the Effluent stations was statistically significant (ANOVA, $p < 0.05$), station 1 being significantly higher than station 3. The pH values of surface water across the sampling points displayed the trend; River Station 1 > River Station 2 > River Station 3. pH values of surface water ranged from 7.23 at River station 3 in the month of February to 7.65 at River station 1 the month of April. The values were also found to decrease downstream. The difference in surface water pH across River stations was statistically significant (ANOVA, $p < 0.05$), with station 1 being higher than station 3. The average pH value of the control station (7.33±0.10) was found to be significantly (ANOVA, $p < 0.05$) lower than that of the established sampling points along the River (Figure 2).

Table 2 shows that effluent temperature also followed the order: Effluent Station 1 > Effluent Station 2 > Effluent Station 3. Effluent temperature ranged between 28.6 and 30.2. The lowest temperature (28.6) was recorded at Effluent Station 3 in the month of February and the highest temperature (30.2) at Effluent Station 3 in March and April. The difference in temperature across the Effluent stations was found to be statistically significant at 95% confidence level.

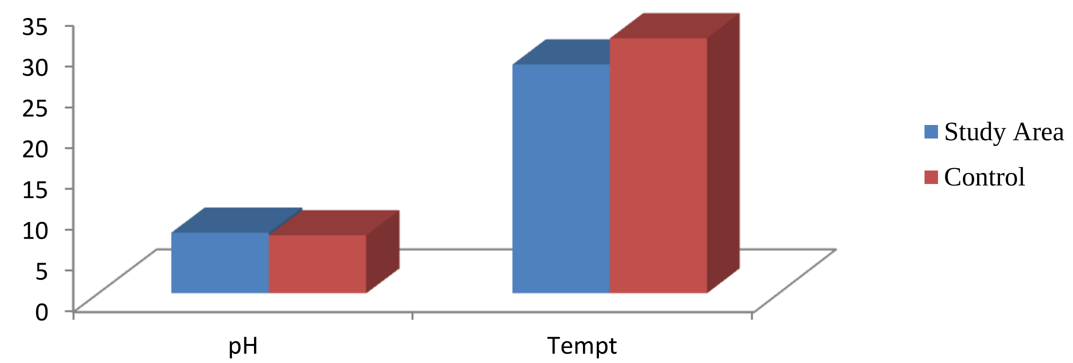
Table-2. Physicochemical Parameters of Effluents from Challawa Industrial Layout surface water of the receiving Challawa River

Parameter	Sampling Month	Effluent Station 1	Effluent Station 2	Effluent Station 3	River Station 1	River Station 2	River Station 3	River Control
pH	February	8.84	8.79	8.76	7.43	7.32	7.23	7.12
	March.	8.89	8.87	8.73	7.54	7.51	7.43	7.12
	April	8.88	8.76	8.72	7.65	7.62	7.33	7.13
	Mean ± SD	8.87 ±0.03	8.81 ±0.06	8.74 ±0.02	7.54 ±0.11	7.48 ±0.15	7.33 ±0.10	7.12 ±0.01
	Range	8.72 -889			7.23 -7.65			
Temperature	February	29.8	29.4	28.6	27.97	27.85	27.56	31.11
	March.	30.2	30.1	28.8	28.22	28.23	28.02	31.21
	April	30.2	30.1	28.6	28.02	28.21	28.11	31.34
	Mean ± SD	30.07 ±0.23	29.87 ±0.40	28.67 ±0.12	28.07 ±1.83	28.07 ±1.86	27.90 ±1.82	31.22 ±0.64
	Range	28.6			27.56			

		-30.2			-28.23			
TDS (mg/l)	February	3790	3650	3404	2443	2342	2237	1884
	March.	3824	3678	3453	2487	2389	2323	1879
	April	3844	3765	3564	2499	2389	2322	1987
	Mean ± SD	3819.33 ±27.30	3697.67 ±59.96	3473.67 ±81.98	2476.333	2373.33 ±27.13	2294 ±49.36	1916.67 ±60.9
	Range	3404 -3844			2237 -2499			
TSS (mg/l)	February	4130	3827	3765	3021	2809	2636	2013
	March.	3966	3753	3667	3067	2897	2543	1908
	April	4212	3987	3786	3143	2875	2435	2012
	Mean ± SD	4102.67 ±99.26	3855.67 ±98.60	3739.33 ±63.51	3077.0 ±6.01	2860.33 ±45.79	2538.00 ±99.59	1977.67 ±60.33
	Range	3667 -4212			2435 -3143			
EC (µs/cm)	February	6343	5834	5632	1843	1802	1792	546
	March.	6543	5854	5612	1873	1887	1863	558
	April	6534	5861	5602	1895	1883	1854	578
	Mean ± SD	6473.33 ±12.96	5849.67 ±14.11	5615.33 ±15.27	1870.33 ±26.10	1857.33 ±47.76	1836.33 ±38.65	560.67 ±16.16
	Range	5602 -6543			1792 -1954			

Effluent temperature at Effluent stations 1and 2 were significantly higher than Effluent station 3. The difference in temperature between Effluent temperatures at Effluent stations 1 and 2 was not statistically significant (ANOVA, $p > 0.05$). Surface water temperature followed the trend River Station 1 > River Station 2 > River Station 3. Surface water temperature ranged from 27.56 at River station 3 in the month of March to 28.23 at River station 2 in the month of April. The difference in surface water temperature across the River stations was not statistically significant (ANOVA, $p < 0.05$). The average surface water temperature at the control station (27.90±1.82) was found to be significantly lower than that of the River stations under study (ANOVA, $p < 0.05$).

Fig-2. Spatial Distribution of the Average concentration of pH, Temperature and Sulphide of surface water in the study area and the control



Electrical conductivity (EC), total dissolved solid (TDS) and total suspended solid (TSS) of the effluents followed the order Effluent Station 1 > Effluent Station 2 > Effluent Station 3 (Table 2). The values ranged between 5602-6543 µs/cm for EC, 3404-3844 mg/l for TDS and 3667-4212 mg/l for TSS. The lowest values were recorded at sampling station 3. While the lowest EC was recorded in April, TDS and TSS were recorded in February and March respectively. The highest values were recorded at Effluent station 1. The highest EC value was observed in February while TDS and TSS recorded their highest in April. Statistical analysis revealed that the differences in all three parameters (EC, TDS and TSS) across the effluent stations were statistically significant (ANOVA, $p < 0.05$). The average EC at effluent station 1 was significantly higher than effluent station 2 and effluent station 3, and that of effluent station 2 significantly higher than effluent station 3. The average TDS value at effluent station 1 was significantly higher than effluent station 3 and that of effluent station 2 also higher than effluent station 3 but the difference in average TDS values between effluent station 1 and 2 was not statistically significant at 95% confidence level. The average TSS value at effluent station 1 was found to be significantly higher than effluent stations 2 and 3. The difference between effluent stations 2 and effluent station 3 was not statistically significant.

Table 2 also shows that the average values of Electrical conductivity (EC), total dissolved solid (TDS) and total suspended solid (TSS) at the established River stations followed the sequence: River Station 1 > River Station 2 > River Station 3. The minimum values of the three parameters (1792 µs/cm for EC, 2237 mg/l for TDS and 2435 mg/l for TSS) were all recorded at sampling station 3 in the month of February while the maximum values (1895 µs/cm for EC, 2499 mg/l for TDS and 3143 mg/l for TSS) were recorded at River station 1in the month of April. The average concentrations of all three parameters (EC, TDS and TSS) at the control station were found to be lower than the average concentration of the three river stations from point source downstream (Fig. 3). The differences were found to be statistically significant at 95% confidence level. Statistical analysis also showed that the difference in average EC values between River station 1, River station 2 and River Station 3 was not statistically significant. However, the difference in the average TDS and TSS values between River station 1, River station 2 and River Station 3 were statistically significant. The average TDS and TSS value at River station 1 were significantly higher than River station 2 and 3. The average TSS value at River station 2 was also found to be significantly higher than River Station 3.

Fig-3. Spatial Distribution of the Average concentration of Electrical Conductivity, Total Dissolved Solid and Total Suspended Solid of surface water in the study area and the control

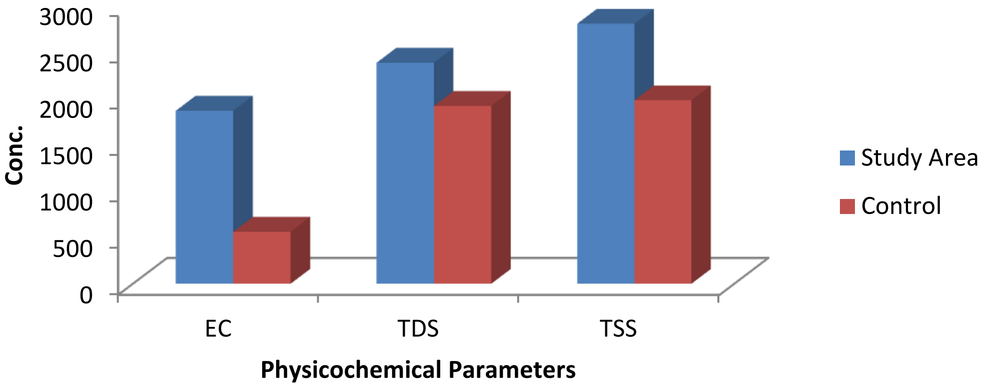


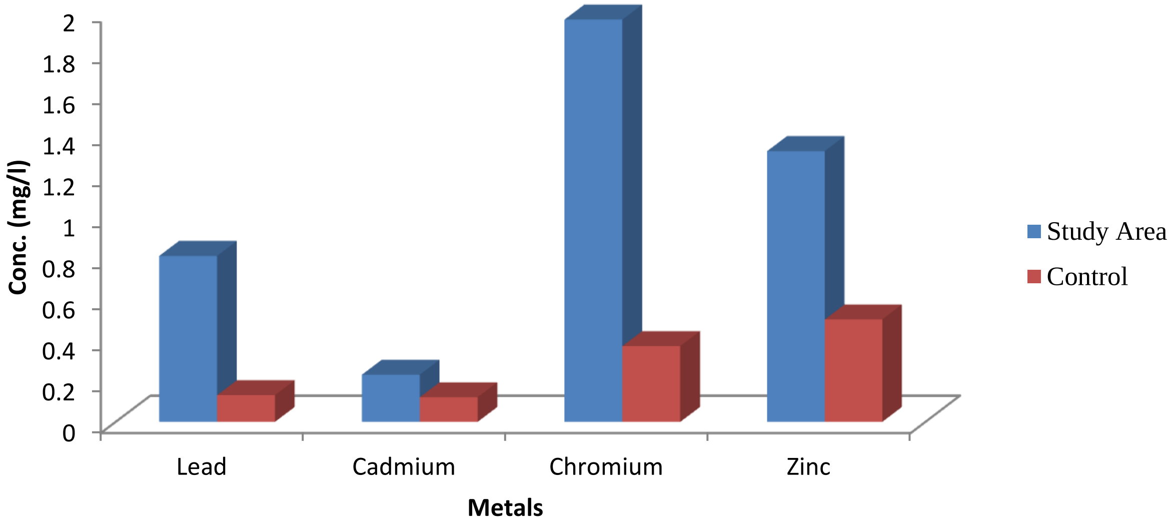
Table-3. Metal levels of Effluents from Challawa Industrial Layout and surface water of the receiving Challawa River

Parameter	Sampling Month	Effluent Station 1	Effluent Station 2	Effluent Station 3	River Station 1	River Station 2	River Station 3	River Control
Lead (mg/l)	February	1.32	1.18	1.06	0.81	0.76	0.72	0.11
	March.	1.41	1.26	1.08	0.86	0.81	0.76	0.12
	April	1.49	0.98	0.86	0.88	0.86	0.81	0.16
	Mean ± SD	1.41 ±0.09	1.14 ±0.14	1.00 ±0.12	0.85 ±0.04	0.81 ±0.05	0.76±0.04	0.13±0.02
	Range	0.86 -1.49			0.72 -1.08			
Cadmium (mg/l)	February	0.87	0.85	0.83	0.25	0.22	0.12	0.12
	March.	0.98	0.96	0.82	0.28	0.24	0.21	0.12
	April	0.98	0.96	0.84	0.31	0.24	0.23	0.13
	Mean ± SD	0.94 ±0.06	0.92 ±0.06	0.83 ±0.01	0.28 ±0,28	0.23 ±0.23	0.19±0.18	0.12±0.12
	Range	0.82 -0.98			0.12 -0.31			
Chromium (mg/l)	February	8.12	0.74	0.64	2.34	1.83	1.68	0.24
	March.	8.78	0.78	0.72	2.46	1.87	1.42	0.26
	April	9.98	0.81	0.74	2.48	1.99	1.56	0.31
	Mean ± SD	8.96 ±0.94	0.78 ±0.03	0.7 ±0.05	2.43 ±0.07	1.90 ±0.08	1.55±0.13	0.27±0.04
	Range	0.64 -9.98			1.42 -2.48			
Zinc (mg/l)	February	3.47	2.85	2.46	0.96	0.94	0.82	0.54
	March.	3.56	2.91	2.48	1.98	1.08	1.06	0.47
	April	3.57	2.94	2.68	2.05	1.45	1.54	0.48
	Mean ± SD	3.53 ±0.06	2.9 ±0.04	2.54 ±0.12	1.66 ±1.66	1.16 ±0.61	1.14 ±0.37	0.50 ±0.04
	Range	2.46 -3.57			0.82 -2.05			

Lead, Cadmium, Chromium and Zinc across the effluent stations displayed the ranges: 0.86-1.49 mg/l, 0.82-0.98 mg/l, 0.64-9.98 mg/l and 2.46-3.57 mg/l respectively (Table 3). The maximum values for all the metals were recorded at effluent station 1 in the month of April and the minimum values at effluent station 3. While the minimum values for Chromium and Zinc where observed in the month of February, Cadmium and Lead recorded their minimum values in March and April respectively. The mean value of each metal across the effluent stations followed the trend: Effluent Station 1 > Effluent Station 2 > Effluent Station 3. The difference in concentration of Lead, Chromium and Zinc across the effluent stations were found to be statistically significant (ANOVA, $p > 0.05$), the Concentration of each of the metal at effluent station 1 being significantly higher than effluent station 2 and effluent station 3. The concentration of Zinc at effluent station 2 was also significantly higher than effluent station 3. However, the difference in Cadmium concentration across the effluent stations was not statistically significant (ANOVA, $p > 0.05$).

Metal concentration of surface water samples ranged between 0.72-0.88 mg/l for Lead, 0.12-0.31 mg/l for Cadmium, 1.42-2.48 mg/l for Chromium and 0.82-2.05 mg/l for Zinc. The lowest concentration of each of the metal was recorded at water station 3 in the month of February except chromium whose lowest value was observed in March. The highest concentrations of the metals were recorded at water station 1 in April. The concentrations thus displayed the trend: River Station 1 > River Station 2 > River Station 3. Statistical analysis revealed that the difference concentration of lead and chromium across the sampling stations were significant (ANOVA, $p < 0.05$), lead concentration at River station 1 being significantly higher than River station 3. Chromium concentration at River station 1 was found to be significantly higher than River station 2 and 3. The concentration at River station 2 was also significantly higher than River station 3. On the other hand, the concentrations of cadmium and Zinc across the River were not statistically significant at 95% confidence level. The difference in metal concentrations between water stations and the controls (Fig. 5) were found to be statistically significant (ANOVA, $p < 0.05$), except for Zinc that displayed difference that were not significant at 95% confidence level.

Fig-4. Spatial Distribution of the Average concentration Lead (Pb), Cadmium (Cd), Chromium (Cr) and Zinc (Zn) of surface water in the study area and the control



4. Discussion

Physical, chemical and biological parameters are commonly used as indicators to determine the quality and overall health of the surface water. Additional information derived from the quality of bottom sediments and point/nonpoint sources of pollution assist in this process. In this study physical and chemical (physicochemical) parameters have been used to assess the pollution potential of effluents from Challawa Industrial layout and the surface water quality status of the receiving Challawa River. The influence of effluents from Challawa industrial layout on the water quality of the river has also been thoroughly evaluated.

4.1. pH

pH has been described as, a measure of the amount of free hydrogen ions in water [15]. Specifically, it is the negative logarithm of the molar concentration of hydrogen ions. Because pH is measured on a logarithmic scale, an increase of one unit indicates an increase of ten times the amount of hydrogen ions. A pH of 7 is considered to be neutral. Acidity increases as pH values decrease, and alkalinity increases as pH values increase [15]. The statistically significant difference in effluent pH observed between Effluent stations 1 and effluent station 3 could be attributed to decrease in temperature and the continuous action of microorganism as the effluent flows down from the confluence point. According to Prasanna and Ranjan [16], Carbon (IV) oxide from the atmosphere or from biological processes in surface water systems tends to lower pH levels very effectively to neutral conditions. The Nigerian Environmental Standards and Regulations Enforcement Agency’s acceptable limit for the discharge of waste water into surface water is between a pH of 6 – 9. The pH of industrial waste water in this study was therefore within the acceptable limit. A lower mean pH value of 7.56 was previously reported for major tanneries in Kano [2].

The significantly lower pH observed at the control station when compared to the other River stations indicates that industrial effluent discharged into the river have significant influence on the overall pH of the River Challawa. The decrease in pH observed downstream from the point source could be attributed to dilution of the discharged effluent as the river flows downstream which is an important part of the much talked about self purification mechanism of flowing surface water bodies. The month of March/April corresponds to the peak of the dry season and river was at its lowest volume. This could account for the high pH values observed in the month in March and decrease observed in April could be due to the onset of the rains. All through the study, pH of surface water from all the stations along River Challawa (Table 2) fell within the pH range (6.5-8.5) assigned by United State Environmental Protection Agency (US EPA), World Health organization (WHO) and the Nigerian Standard for Drinking Water Quality (NSDWQ) as standard pH for water, making it suitable for portability with respect to pH [17]. Although not definitive, pH of aquatic system is an important indicator of the water quality and the extent of its pollution. The measurement of the pH of surface waters is an essential part of water quality assessment because many pollutants increase in toxicity with changes in pH. Examples of this phenomenon are the dissolution of metal ions in acidic (low pH) waters and the shift of ammonium ions to un-ionized ammonia in basic (high pH) waters. The pH of water is important because taste, corrosiveness, and the effectiveness of chlorination and coagulation in treatment processes are affected. Aquatic ecosystems also are influenced by pH. In general, pH alone is not a problem, but the combination of pH with temperature, dissolved oxygen, and the presence of various ions could pose a significant problem. Some compounds are more toxic to the aquatic organisms at different pH values. For example, the toxicity of nickel cyanide increases as the pH value decreases [15]. If the surface water pH shift too far either way from the acceptable range, highly mobile aquatic organism tend to migrate to safer environments while the life of sedentary organisms are susceptible to loss. At lower pH, sulphides present in tannery waste water begin to evolve as hydrogen sulphide resulting in toxic conditions [2]. Mean pH values ranging from 7.21±0.02 to 10.46±0.01 have previously been reported for different sampling points along Challawa River [18]. A range of 7.45 - 8.63 have been reported for drains receiving water from tanneries in India s[19].

4.2. Temperature

The temperature of water influences the chemical and biological processes and the aquatic life present in water bodies. The amount of sunlight, rainfall, air temperature, ground water discharge, and thermal point sources all influence the surface water temperature. The average temperatures of the effluents recorded in the study (Table 2) were found to be within the permissible limit. The maximum permissible limit set by the Nigerian Environmental Standards and Regulations Enforcement Agency (NESREA) for tanning, leather finishing and other industries stipulate that temperature must be less than 40^0C within 15 meters of out fall. The statistically significant difference in effluent temperature observed between effluent station 1 and effluent station 3, and between effluent station 2 and effluent station 3 could be attributed to the influence of the ambient temperature as well as the dilution of the effluent as it flows down the drains. It is important to note that at the confluence point, effluent from different industries mix together and flow downstream.

The average surface water temperatures (Table 2) were found to be within the WHO standards of 30 ^{0}C – 35^0C for drinking water quality [20]. The significantly lower temperature recorded at the control station when compared to the other three river stations from the point source downstream suggest that effluent from industries around Challawa industrial area have significant influence on the quality of Challawa River. The highest temperature of surface water recorded in the month of April could be explained in terms of the high intensity of sun light that characterized the onset of the rains in the year under study. At this period the River was still at its lowest volume. Adedokun and Agunwamba [12] reported similar temperatures ranging from 29.0 to 31.3°C for River Challawa. Mean temperatures ranging from 23.27±0.06 to 26.15±0.01 have also been reported for different sampling points along Challawa River[18]. A range of 18.6 - 30.3^0C have been reported for drains receiving waste water from tanneries in India [19]. A mean temperature of 28.5°C was reported for downstream area of River Galma while 25.7°C was recorded for upstream area of river Galma in 2011[21]. A range of 18.6 - 30.3^0C have been reported for drains receiving waste water from tanneries in India [19].Temperature impacts both the chemical and biological characteristics of surface water. Increase in temperature leads to increase in solubility. At high temperatures TDS is increased as more solute goes into solution. It also affects how much oxygen the water can hold. Increased water temperature lowers the amount of dissolved oxygen available for the aquatic life present and promotes excessive growth of aquatic plants and algae. Also, the toxicity of pollutants tends to intensify with an increase in temperature [15]. Temperature is therefore important to aquatic plants and animals and the overall health of the water [17].

4.3. Electrical Conductivity, Total Dissolved Solids and Total Suspended Solids

Electrical conductivity (EC), total dissolved solid (TDS) and total suspended solid (TSS) values for effluents were all found to decrease significantly from effluent station 1 to effluent station 2 and then effluent station 3 (Table 2). The decrease in TSS could be attributed to continuous deposition as the effluent flow down the canal. Decrease in temperature in the same direction may account for decrease in TDS as most solute tend to come out of solution as temperature decreases and decrease in dissolved solutes on the other hand could be responsible for the decrease in EC values. Electrical conductivity and total dissolved solutes of effluents were higher than the WHO maximum permissible limit of 1000 µs/cm and 2000 mg/l [22] for EC and TDS respectively. Mean effluent conductivity and total dissolved solute values of 3020 µs/cm and1537.50 mg/l respectively were previously recorded for major tanneries in Kano [2] and a range of 1554 – 11410 µs/cm and 585.00 -7250 .00 mg/l respectively recorded for tannery in Kano metropolis [22]. The effluent limitation standard for TSS in tanning and leather finishing industries in Nigeria is 25 mg/l. The mean values of TSS recorded in this study across the effluent stations were far above this standard. Lower mean effluent TSS value of 1217.35 µs/cm was previously recorded for major tanneries in Kano [2] and a range of 1026.00 - 3365.60 mg/l recorded for tanneries in Kano metropolis [22].

All three parameters (EC, TDS and TSS) at the established river stations recorded lowest values in the month of April (Table 2). This observation could also be explained in terms of the fact that April corresponded to the peak of the dry season in the year under study and at that period, the River was still at its lowest volume and the sun at its peak. The decrease concentration of the parameters downstream from the point source could also be attributed to dilution as well as the gradual settling of the suspended matter. The statistically significant difference in concentration of all the parameters between the control station and the study area indicate that effluent discharge from Challawa industrial area has significant influence on the water quality of the River.

In the present study, the conductivity values were found to be above the recommended standard of 750 µS/cm [17], hence with respect to electrical conductivity, the water is not safe to be used for domestic and agricultural purposes. Similar electrical conductivity ranging from 93 µS/cm to 120 µS/cm in the downstream area and from 80 µS/cm to 103 µS/cm in the upstream area of River Galma was previously reported [17]. Conductivity is the ability of a substance to conduct electricity. The conductivity of water is a more-or-less linear function of the concentration of dissolved ions. Conductivity itself is not a human or aquatic health concern, but because it is easily measured, it can serve as an indicator of other water quality problems. If the conductivity of a stream suddenly increases, it indicates that there is a source of dissolved ions in the vicinity. Therefore, conductivity measurements can be used as a quick way to locate potential water quality problems. The high conductivity values recorded in this study is therefore indicative of the presence of high concentration of dissolved ions solutes and could be attributed to the attributed to the large amount of chemicals used in the tanning process [2]

The total dissolved solid of water samples from the point source downstream (water station 1, 2 and 3) were found to be above the WHO standards of 2000 mg/l [22]. The average TDS value at the control station was however within the acceptable limit. A range of 34.67 – 215.67 mg/l was previously reported for River Challawa [18]. Adedokun and Agunwamba [12] recorded 2843mg/l and 743 mg/l for dry and wet season respectively at River Challawa. Total dissolved solids (TDS) in water consist of dissolved mineral salts that change the physical and chemical properties of the water. According to Reddy and Subba [23] cited in Bernard and Ogunleye [22], high TDS value increases the salinity of water and thus may render it unhealthy for drinking and irrigation purposes. Although fish can acclimatize slowly to higher TDS concentrations than they are accustomed, they cannot survive a sudden exposure to a high TDS concentration [24]. This makes the discharge of wastewater into surface water harmful. Consumption of water with high concentrations of TDS has been reported to cause disorders of alimentary canal, respiratory system, nervous system, coronary system besides causing miscarriage and cancer. A high concentration of TDS in water is a concern for water purveyors because it alters the taste. High TDS concentrations also exert osmotic pressure in water purification systems in hospitals and industries and exert osmotic pressure on the stream ecosystem [24].

Total Suspended Solids (TSS) ranging from 27.38 mg/l to 58.55 mg/l with a mean value of 39.24±9.44 mg/l in the dry season and from 61.27 mg/l to 78.24 mg/l with a mean value of 69.04±4.19 mg/l in the wet season reported for River Galma (Diya' udden *et al.,* 2014) were generally lower than the values obtained in this study. Wakawa, *et al.* [18] reported a range of 167.00 – 426.67 mg/l for river Challawa. 393 mg/l and 240 mg/l were also measure for River Challawa at the point source for dry and wet season respectively [12]. The total suspended solid found in water is the sum of the total quantity of insoluble matter contained in the water. According to Holmbeck-Pelham and Rasmussen [25], TSS concentrations in the range of 25-80 mg/l represent moderate water quality. An average concentration of 25 mg/l has been suggested as an indicator of unimpaired stream water quality. Some states use 50 mg/l as a screening level for potential impairment to water bodies. TSS originates mainly from effluent discharges, storm water runoff, stream bank and channel erosion, dead plant matter, plankton, and re-suspension of sediment into the water column. High concentration of TSS adversely affects surface water's ecosystem. It reduces the penetration of sunlight into surface water and thus reducing the amount of oxygen that could be assimilated into the given water body [12]. The reduction in penetration of sun light also results in the decrease of algal growth, and low algal productivity can reduce the productivity of aquatic invertebrates, a food source of many. Fish and shellfish can be injured or killed from the TSS by abrasive injuries, clogging gills and respiratory passages, and by blanketing the bottom, killing eggs, young, and destroying spawning beds. The waters become cloudy and the system can develop noxious conditions, reducing the aesthetic value of the waters. Other pollutants, such as phosphorus and petroleum hydrocarbons, adsorb or bond to the particles therefore magnifying the impact the solids have on the surface water quality. It also interferes with the treatment processes for water purveyors [24]. It was observed that, suspended solid contents were higher than the dissolved solids in all effluent and river stations. It may be attributed to turbulence in the water bodies during sampling or probably because the suspended solids are largely non-settleable. The observation was in agreement with the finding of Wakawa, *et al.* [18] for River Challawa and Osibanjo, *et al.* [26] for River Ona and River Alaro in Oluyole Industrial Estate, Ibadan, Nigeria.

4.4. Metal Concentration of Effluent and Surface Water

The results obtained in the present study (Table 2) showed that lead, cadmium, chromium and zinc content of effluent across the sampling stations decrease significantly from effluent station 1 to effluent station 3. Effluent temperature was found to follow the same trend and may thus account for this observation. Gravitational deposition down the drain may also account for the reduction in metal levels. The concentration of each of the metal was found to be above the effluent limitation standard of 0.1 mg/l for lead, and cadmium, 0.5 mg/l for chromium and 1.0 mg/l for zinc as established by the Nigerian Environmental Standards and Regulations Enforcement Agency (NESREA) for tanning and leather finishing industries. The effluents thus constitutes serious environmental hazard. The mean effluent cadmium and chromium concentrations were found to be above both the long term trigger values (LTV) of 0.01 mg/l and 0.10 mg/l respectively and short term trigger values (STV) of 0.05 mg/l and 1.00 mg/l set by the Australian and New Zealand Environment and Conservation Council for irrigation water [27]. The implication therefore is that effluent from the drain in Challawa industrial layout is not fit for irrigation purposes and thus poses a serious risk with respect to Cadmium and chromium poisoning. The STV and LTV values have been developed to minimize the build-up of contaminants in surface soils during the period of irrigation and to prevent the direct toxicity of contaminants in irrigation waters to standing crops. The mean effluent zinc concentration was observed to be below the short term (5.00 mg/l) but above the long term (2.00 mg/l) trigger value indicating that the use of the effluent for irrigation does not pose immediate risk but over time it will accumulate to toxic level. However the use of the effluent for irrigation does not pose any risk with respect to lead contamination as the mean value was found to be below both the long term (2.00 mg/l) and short term (5.00 mg/l) trigger values of the Australian and New Zealand Environment and Conservation Council limits for irrigation water Australian and New Zealand Environment and Conservation Council (ANZECC) [27] reported mean effluent concentration of 2.297, 1.051 and 2.986 for Chromium, lead and zinc for effluent discharged into water supply in kano, In their evaluation of industrial effluent content in Kano Bernard and Ogunleye [22] reported values ranging from 0.67 mg/l to 3.10 mg/l for lead and 3.33 to 5.79 mg/l for Chromium.

The concentration of the metals in surface water of River Challawa was found to decrease significantly downstream from the point source. This observation could be attributed to dilution cum self purification mechanism of the river system. The metals concentrations at the control station was significantly lower than River stations 1, 2 and 3 suggesting that the effluent from Challawa industrial area has significant influence on the heavy metal profile of the river. A significant ($p < 0.01$) positive correlation was observed between cadmium and lead ($r = 0. .824$) cadmium and chromium ($r = 0. 872$) and, between cadmium and zinc ($r =0. 882$). Lead was found to display a significant positively correlation with chromium ($r = 949$) and zinc ($r = 0. 772$). Chromium also displayed a significant positive correlation with zinc ($r = 0. .801$). These observations indicate that an increase in cadmium concentration is associated with increase lead, chromium and zinc concentrations. An increase in lead concentration is also associated with increase in chromium and zinc concentrations. Thus suggesting that same source is responsible for the presence of these metals at the concentration determined. Zinc content of River Challawa observed in this study was found to be lower when compared to World Health Organization (WHO) and the Nigerian Standard for Drinking Water Quality (NSDWQ) of 3 mg/l for portable water [28, 29]. The mean zinc concentration was also below both the short term trigger value (5.00 mg/l) and the long term (2.00 mg/l) for irrigation water [27]. The river therefore poses no risk either short or long term at present concentration with respect to zinc contamination when used for drinking or irrigation purposes. Zinc concentration observed in this study is in agreement with Dan'azumi and Bichi [30] who reported zinc concentration ranging from 0.247 to 2.227 mg/l for River Challawa. Mean value of 2.72 ± 0.57 mg/l was reported for lower river Niger drainage in North central Nigeria [31]. Zinc is a natural component of the earth crust. Most of the zinc compounds in nature are soluble in water. The metal is essential for plants and animals but at high concentrations it becomes toxic. The Long-term trigger values and Short-term trigger values for zinc was therefore set to minimize the potential phytotoxicity of irrigation waters due to the presence of zinc. Zinc is an intestinal irritant, and the first sign of Zinc poisoning is usually intestinal distress. This includes vomiting, stomach cramps, diarrhea, and nausea. Further symptoms of Zinc poisoning are low blood pressure, urine retention, jaundice, seizures joint pain, fever, coughing, and a metallic taste in the mouth as well as induced Copper deficiency [32, 33]

Lead content of River Challawa observed in this study was found to be higher when compared to World Health Organization (WHO) and the Nigerian Standard for Drinking Water Quality (NSDWQ) of 0.01 mg/l for portable water [28, 29], the water is thus not fit for drinking purposes. As observed in table 2, lead level was found to be below both the long term (2.00 mg/l) and short term (5.00 mg/l) trigger values of the Australian and New Zealand Environment and Conservation Council limits for irrigation water [27] The river therefore poses no significant risk with respect to lead contamination when used for irrigation. Lead is a natural constituent of the earth crust. It is the most abundant among the heavy metals with an atomic number >60. Given the evidence from solution culture of potential direct lead toxicity to plants, the long-term trigger values and Short-term trigger values have been set in order to minimize these risks. Dan'azumi and Bichi [30] reported concentrations ranging from 0.095 to 0.084 for River challawa, Kano, Nigeria and 0.039 to 0.256mg/l for streams that receive effluents from different categories of industries in Nakawa - Ntinda industrial area of Kampala, Uganda [33, 34]. Oronsaye, *et al.* [35] reported a lower range of 0.05 to 0.07 mg/l for Ikpoba river dam, Benin City, Nigeria. Lead exposure in young children has been linked to learning disabilities. Lead affects both the male and female reproductive systems. In men, when blood lead levels exceed 40μg/dl, sperm count is reduced and changes occur in volume of sperm, their motility, and their morphology. A pregnant woman's elevated blood lead level can lead to miscarriage, prematurity, low birth weight, and problems with development during childhood [36]. Kidney damage occurs with exposure to high levels of lead. In acute poisoning, typical neurological signs are pain, muscle weakness, paraesthesia, and, rarely, symptoms associated with encephalitis [37].

Chromium content of River Galma observed in this study was also found to be higher than the World Health Organization (WHO) and the Nigerian Standard for Drinking Water Quality (NSDWQ) of 0.05 mg/l [28, 29]. The mean chromium concentration of River Challawa was found to be both the long term (0.10 mg/l) and short term (1.00 mg/l) trigger values of the Australian and New Zealand Environment and Conservation Council limits for irrigation water [27]. This implies that the river is not fit for domestic or agricultural purposes and thus poses significant risk with respect to chromium contamination. Chromium is known in all oxidation states from -2 to +6, with +3 (chromic) and +6 (chromate) being the most common. There is no evidence that the metal is essential to plants, although traces of it are essential for humans and animals. In general, there should be few problems associated with discharges to land of wastewaters (e.g. from tanneries) containing chromium (III) because this form of chromium is reported to be relatively non-mobile [27]. Studies with nutrient solutions indicate that there may be some direct phytotoxic effect on irrigated crops of chromium in irrigation waters. Concentrations of 1–10 mg/L in nutrient solutions reduce crop yield, depending on the tolerance of different plant species and there is limited evidence that chromium (III) and chromium (VI) in nutrient solutions are about equally available to plants. It is therefore inappropriate according to Australian and New Zealand Environment and Conservation Council to set a guideline based on total chromium or chromium (III) due to the lack of evidence that chromium (III) poses a significant environmental or phytotoxic threat. Guidelines are therefore set for the chromium (VI) ion in irrigation waters based on the revised South African irrigation water quality guidelines [27]. Higher concentration ranging from 0.213 to 0.924mg/l was reported for River challawa, Kano, Nigeria [30] and 0.33 to 1,56mg/l for River Warri, Niger Delta, Nigeria [38]. Chromium concentration ranging from 0.0365 mg/l – 0.0865 mg/l was reported for surface water around Gboko abattoir [39]. Lower chromium concentration ranging from 0.01 to 0.14 mg/l was reported for Warri River [40] and 0.11 to 0.17 mg/l for River Ikpoba, in Niger Delta, Nigeria [38]. A mean value of 2.08 ± 1.27 mg/l was reported for lower river Niger drainage in North central Nigeria [31].

Cadmium content (Table 2) was found to be higher when compared to World Health Organization (WHO) and the Nigerian Standard for Drinking Water Quality (NSDWQ) of 0.003 mg/l for portable water [28, 29]. Drinking or use of water from River Challawa for domestic purposes thus poses serious toxicological risk with respect to cadmium intoxication. The mean cadmium concentration of River Challawa was above both the long term (0.01 mg/l) and short term (0.05 mg/l) trigger values of the Australian and New Zealand Environment and Conservation Council limits for irrigation water [27]. It follows therefore that the river is not fit for irrigation purposes as cadmium uptake by plants and subsequent transfer into the food chain cannot be completely ruled out. Salts of cadmium with strong acids are readily soluble in water. Cadmium is toxic to both animals and plants at low concentrations, research also indicates that carcinogenity also may be a possibility. Chloride concentration in irrigation water is important in controlling cadmium uptake by plants. Cadmium in nutrient solutions is phytotoxic to a range of plants at levels ranging from 0.1 mg/L to 1 mg/L [41], but human and animal health concerns from ingestion of cadmium-contaminated crops are triggered at sub-phytotoxic concentrations. The Long term Trigger Value and Short term Trigger Value have therefore been set to prevent the uptake of cadmium into crops that may pose a threat to animal and human health. Cadmium accumulates in the kidney and liver causing kidney dysfunction and liver failure, interferes with the metabolism of Calcium and Phosphorus, causing painful bone diseases, in addition to being a teratogenic and carcinogenic agent. Eating food or drinking water with high Cadmium concentration irritates the stomach causing vomiting and diarrhea. Chronic exposure can also cause irreversible damage to the lungs. A higher concentration of cadmium ranging from 0 to 0.39 mg/l and from 0.22 to 0.52 mg/l were reported for Warri River, Nigeria by Ayenimo, *et al.* [40] and Owamah [38] respectively. Our observation is in agreement with Owamah [38] who reported a range of 0.01to 0.05 for River Ikpoba in Niger Delta, Nigeria. A mean value of 0.05 ± 0.02 mg/l was reported for lower river Niger drainage in North central Nigeria [31].

5. Conclusion

The direct discharge of industrial effluents into bodies of water has become a growing environmental problem of global concern. The evaluation of the pollution potential of effluent from Challawa industrial layout, Kano revealed that the effluent failed to meet NESREA limits for discharge into surface water and the Australian and New Zealand Environment and Conservation Council limits for irrigation water. It was also observed that surface water of the receiving River Challawa failed to meet World Health organization (WHO) and the Nigerian Standard for Drinking Water Quality (NSDWQ) standards for portable water. The study showed clearly that effluent had significant adverse influence on the overall surface water quality of the river. Extraction of the effluent for irrigation purposes or surface water of the river for domestic or industrial purposes poses serious toxicological risk to human health. It was therefore recommended that, the discharge of industrial effluent without adequate treatment should be discouraged. Regulatory agencies should therefore rise up to their statutory responsibility of enforcement by compliance monitoring.

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