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IMPACT OF INDUSTRIAL WASTE WATER ON SELECTED HEAVY METALS LEVELS OF RIVER RIDO, KADUNA SOUTH, KADUNA STATE, NIGERIA

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Abstract:

Heavy metal is a major environmental threat, hence the need for regular monitoring in order to identify contaminant sources, types and levels of concentrations for the purpose of policy formulation to promote sustainable wastewater management and treatment infrastructure. Thus, this study aimed to examine the impact of industrial effluent on selected heavy metal levels in River Rido, southern Kaduna, and Kaduna State, Nigeria. Eight heavy metals, Cadmium (Cd), Lead (Pb), Arsenic (As), Cobalt (Co), Chromium (Cr), Manganese (Mn), Mercury (Hg) and Iron (Fe) were analysis. The study showed that Pb, Fe, Cd and Mn at the discharge points and points downstream of Rido River were higher than permissible limits for drinking water, while As and Hg were within margin, although higher than levels at the control point. Results of student t test revealed significant difference in the levels of heavy metal concentration between effluent discharge points and control point as well as between control point and points downstream of River Rido, an indication of increased concentrations at effluent discharge point and areas downstream of the study area. More so, significant differences in the levels of heavy metals between discharge points, points downstream of the study area and permissible limits for drinking water as given by WHO (2011) was also observed at 0.05 level of confidence. There is need to formulate and adopt enforceable policies on wastewater management and treatment facility in the study area in order to minimize environmental pollution associated with wastewater from Northern noodles and the Petroleum Corporation (NNPC).

Keywords: Industrial effluent, Heavy metal, surface water, contamination, wastewater discharge

Introduction

Water pollution from industrial activities remain a global challenge in the developing countries due to population explosion, unregulated urban land use activities, weak institutional framework and policies on sustainable waste management. The issue of sustainable resource management is central in the 2030 Agenda for Sustainable Development which acknowledges the importance of water quality for the overall health of the environment and the mankind. The reason is mainly because water-related diseases are still prevalent and widespread in developing countries where surface water remain an important source of water supply for most rural and semi-urban settlements following poor access to portable water sources from urban water supply scheme. A study by WHO and UNICEF shows that Globally, more than 785 million people did not have access to basic water services, and more than 884 million people did not have safe water to drink (WHO/UNICEF, 2019). Developing countries are worst hit, as according to United Nations World Water Assessment Programme report, several water-related diseases, including cholera and schistosomiasis, remain widespread across many developing countries, where only a very small fraction (in some cases less than 5%) of domestic and urban wastewater is treated prior to its release into the environment (WWAP, 2017). In addition, CDC (2021) estimated that 446,000 children younger than 5 years old die from diarrhea, mostly in developing countries, and this amounts to 9% of the 5.8 million deaths of children younger than five (5). Heavy metals are known to be persistent in water pollution depending on the predominant land use activities. Where this is the case, health challenges ranging from genetic mutation, deformation, cancer to kidney problems etc, have been linked to pollution by heavy metals (Jiang *et al*., 2016; Antoniadis *et al*., 2017a; Antoniadis *et al*., 2017b; Adeyi and Babalola, 2017; Olagunju, *et al.*, 2020). Human settlements, industries and agriculture land use are the major sources of water pollution and study has revealed that 80 percent of wastewater from this sources is discharged into water bodies untreated, and WWAP, (2017) has shown that industry is responsible for dumping millions of tonnes of heavy metals, solvents, toxic sludge and other wastes into water bodies each year. Similar observations have been reported of Nigerian rivers (Fakayode 2005; Kanu and Achi 2011; Osibanjo et al 2011; Ado et al., 2015; Chukwu, 2017; Gbarakoro et al., 2020; Wokoma and Edori 2020). These authors agreed that except for a few regions, most urban areas in Nigeria do not have any central sewerage system or sanitary excreta disposal system. In a similar study, UN-HABITAT, (2009) reported that close to 70% of untreated industrial wastes in developing countries is discharged into water where they contaminate existing water supplies.

Exacerbating the problem of surface water pollution from industrial activities, is the challenges of urban expansion, urban flooding and climate change. Kaduna State is fast growing and has over the years witnessed unprecedented increase in urbanization and industrialization. In 2006, Kaduna State had a population of 6.1 million people, next only to Kano and Lagos States. It is projected that at 3.18 per cent growth rate, this population would reach 12.96 million by 2050 (Kaduna State Infrastructure Master Plan, 2018). This population increase has implications for waste generation and management. Industrialisation is an important driver of economic development and can be significant in alleviating poverty (United Nations Industrial Development Organization, 2020; United Nations Department of Economic and Social Affairs). However, industrialisation can also leads to water pollution, and this is particularly prevalent in developing countries, which often lack control legislation and prevention infrastructure (Strokal, et al. 2021; Damania et al., 2019; Iordache et al., 2020). Waste water discharge by industrial sectors is reported to be responsible severe ecological degradation in the surface water environment and has yielded significant health problems (Chen et al., 2019; Genc et al., 2019; Xing et al., 2020). Others have also reported elevated temperatures (Boyle & Fraleigh, 2003; Canobbio, et al., 2009) and nutrient levels, such as nitrate (Chen, et al., 2009; Hur et al., 2007), ammonium/ammonia (Boyle and Fraleigh, 2003; Gafny et al., 2000), and phosphate (Birge, *et al.*, 1989; Chen *et al*., 2009). Reaches downstream of effluent outfalls are also frequently characterised by depleted dissolved oxygen levels (Birge et al., 1989; Matamoros and Rodríguez, 2017). Currently, environmental laws in many countries require wastewater treatment plants to enhance these natural purification processes (e.g. nutrient uptake, increasing dissolved oxygen, and decreasing biological oxygen demand), but treatment standards and technology vary widely across the globe (Angelakis and Snyder, 2015; Libralato, *et al*., 2012; Hamdhani *et al.*, 2020), while for most countries, even those these technologies exist, effluents are ill-treated before disposal into freshwater courses (Edokpayi *et al.*, 2017; Chandan *et al.*, 2017). This is the case with River Rido, a major source of water supply in Kaduna South, which receives waste water from the northern noodles and the Kaduna refinery.

Materials and Methods

Study Area

The River Rido which drains the study area is located in the southern part of the Kaduna metropolis in Chikun Local government area and lies geographically at Latitude $9^{0}03^{'}$N and $11^{0}32^{'}$N north of the equator and Longitudes $6^{0}05^{'}$E and $8^{0}38$’E East of the Greenwich meridian. The river is strategic because over the years, it has become a receiving point for effluent from major industries in the state as well as used for irrigation purposes during the dry season. Minor fishing activities are also carried on by the local population in the area. The communities around the River practice arable farming of crops like vegetables along the river channels.

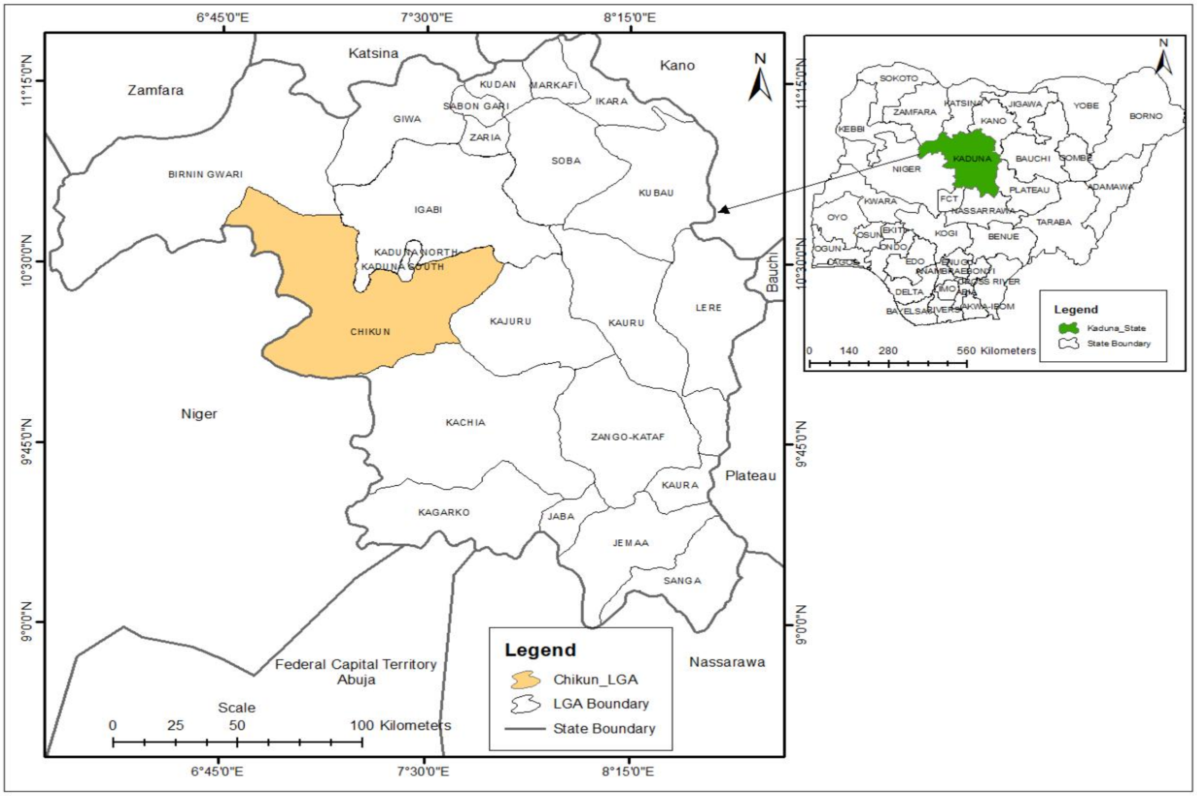

Fig. 1: The Study Area (Kaduna State Showing Chikun LGA)
Source: KADGIS (2018)

The climate of Chikun Local Government Area is characterized by distinct wet and dry seasons. The two seasons are controlled by two prevailing air masses blowing over the area at different periods during the year (Oguntoyinbo, 1983). The tropical continental air mass brings dry season while the tropical maritime air mass brings wet season. The wet season begins in April and ends in October, while dry season is from November to March. The average annual rainfall in the study area ranges between 1000mm and 1350mm respectively. The study area experiences high temperature all year round which is tipical of the tropics. The mean daily temperature is between 27-33^{0}C (Butu *et al.*, 2020), while cold season span from between Octobers to February (Ogbeni, 2007). Vegetation around river areas often shows zonation in the plant species present as the environment changes from permanently or seasonally aquatic habitats in the waterway channel and floodplain wetlands to frequently flooded habitats along the banks and close to the channel, to drier habitats at the edge of the floodplain (Saad *et al.,* 2001).

Data types and Collection

A total of eleven (11) sampling points were established along the river, based on accessibility to sampling points. Water samples were collected at 100m above the Northern Noodles and Nigerian National Petroleum Corporation (NNPC), which is considered control point, Northern Noodles and Nigerian National Petroleum Corporation Refinery discharge points. Other sampling points were points downstream of River Rido, marked as D, E, F, G, H, I, J and K. Sample collection was done at the depth of 30cm directly into clean amber bottles at the interval of 100metres. Heavy metals analyzed were Cadmium (Cd), Lead (Pb), Arsenic (As), Cobalt (Co), Chromium (Cr), Manganese (Mn), Mercury (Hg) and Iron (Fe). These metals were chosen because they are commonly found around industrial residential land-use activities. More so, their high toxicity rate are known to cause various health related problems such as liver and kidney failure, cells and tissue injury etc. Water sampling was carried out from December to February, 2020, hence making it thirty three (33) samples from eleven (11) sampling points.

Sampling methods

The sampling bottles were disinfected with methylated spirit and thoroughly rinsed with the sample water to ensure no contaminant is introduced into the sample as recommended by APHA (1995). The water samples were collected using the grab sampling method by dipping a 250 ml plastic bottle 30 cm below the water surface at each selected sampling point. The sample bottles were labelled with the appropriate source and date of collection before being transported to the laboratory of National Agency for Food and Drug Administration and Control (NAFDAC), Kaduna Laboratory Services, where they were stored in the refrigerator for analysis.

Sample Preparation

One hundred milliliters (100ml) of the water sample was placed in a beaker, to which 1ml of high purity nitric acid was added. The beaker was heated for approximately two hours on a hot plate covered with a watch glass at a temperature just below boiling. After which it was left to cool to room temperature, it was then be transferred to a plastic container and made up to 100ml with a clean water, and be used for analysis. The elements to be measured was also added to the water to create a spike-and recovery test solution. For elements present in high concentration, dilution test solutions were prepared by diluting 10-fold with 1 % nitric acid solution.

Preparation of Standard Curve

The standard curves for the heavy metals was prepared bearing in mind that these elements occur in trace concentration. Standard solutions was be prepared from 1000 parts per millions (ppm) stock solution. One milliliter of the 1000ppm stock solution was pipetted into a 100 ml volumetric flask and made up with distilled water. This solution was 10 ppm of the solution. From this solution, standard solutions of 0.2, 0.4, 0.6, 0.8 and 1ppm was be prepared by taken 0.2, 0.4, 0.6, 0.8 and 1ml portions into 10ml volumetric flasks and made to mark. These were then run in the Air Acetylene flame and standard curves for the various elements were obtained.

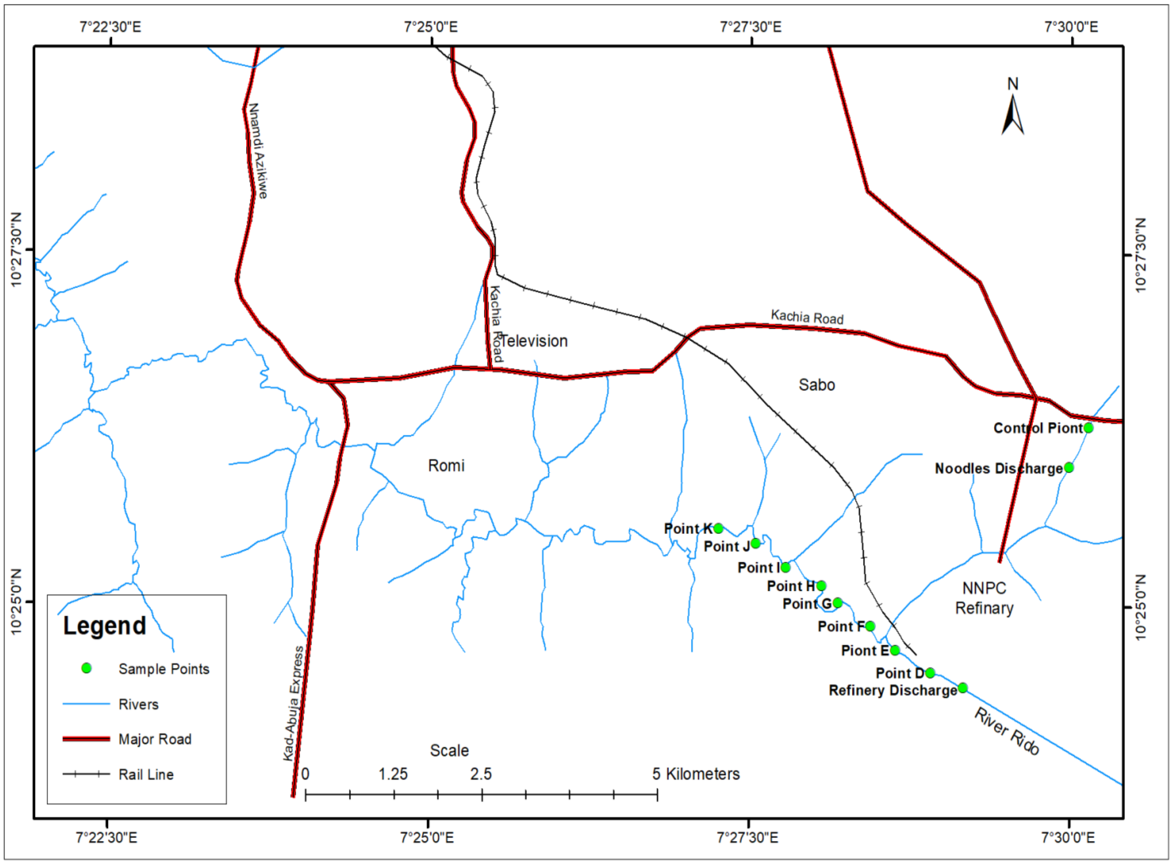

Figure 2: Sampling Locations

Laboratory Analysis

Shimadzu's ICPE-9000 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP AES) was used for the analysis of chemical contaminants. Analytical conditions are shown on Table 1 as stipulated by Shimadzu (2016). The justification for the choice of this technique is based on availability, cost and also that ICP AES has the capacity to identify a particular element using multiple wavelengths, which gives it a broad spectrum of usage among other analytical techniques. The prepared standard solutions and the water samples were injected into the ICP AES equipment after all the analytical conditions are set and the instrument is ready for analysis. After analysis, calibration curves were created and the peak concentration for the samples was correlated automatically with the calibration curve and the element concentration determined. The analysis was carried out at the National Agency for Food and Drug Administration and Control (NAFDAC).

Table 1: ICPE-9000 Analytical Conditions for operation of the equipment

S/N	Instrument	ICPE-9000
1	Radio Frequency	1.2 (kW) Coaxial
2	Power	HVG-ICP 1.0 (kW) UAG-1
3	Cooling Gas	10 (L/min)
4	Plasma Gas	0.6 (L/min)
5	Carrier Gas	0.7 (L/min)
6	Sample introduction	Coaxial Nebulizer (UAG-1, HVG-ICP
7	Sample Aspiration	0.6 (mL/min) Coaxial 1.5 (mL/min) UAG-1 4.0 (mL/min) HVG-ICP
8	Misting Chamber	Cyolone Chamber
9	Attached	Mini Torch
10	Instruments View	Axial

Heavy Metal Pollution Index

Water quality Index computation WQI: The WQI model as adopted by Parastar *et al*. (2015) was utilised. The approach makes use of just nine parameters for the computation of the water quality index of a sample of water. The empirical relationship upon which the WQI model is based is given in equation 1

$$QWI = \sum_{i=1}^{n} w_i - q_i - - - - - - - - - - - - 1$$

Where *n* is the number of variables or parameters,
*w*i is the relative weight of the *i*th parameter and
*q*i is the water quality rating of the *ith* parameter.

The unit weight (*w*i) of the various water quality parameters are inversely proportional to the recommended standards for the corresponding parameters. According to Brown, *et al.,* (1972), the value of *q*i is calculated using the following equation (2).

$q_i = 100[\frac{V_i - V_{id}}{S_i - V_{id}}]$---------------------------2

Where Vi is the observed value of the ith parameter,
Si is the standard permissible value of the ith parameter and
Vid is the ideal value of the ith parameter in pure water.

All the ideal values (Vid) are taken as zero for drinking water except pH and dissolved oxygen (Tripaty and Sahu, 2005). For pH, the ideal value is 7.0 (for natural/pure water) and a permissible value is 8.5 (for polluted water), while for Do, Vi is given as 14.6 mg/L.

Calculation of unit weight

The Unit weight (Wn) to various water quality parameters are inversely proportional to the recommended standards for the corresponding parameters. It is given as

$Wn = k/S_n$---(3)

Where wn = unit weight for nth parameter
Sn = standard permissible value for nth parameter
k = proportionality constant.

K was determined by dividing a unit value (1.00) by the standard permissible value of parameter as shown in equation 4

$K = [1/(\sum \frac{1}{Sn=1,2,\dots n})]$…………………………………..(4)

The parameters used in thus study and their computer weights are presented in Table 1 while Table 2 shows the ranges of WQI, the corresponding status of water quality and their possible uses.

Table 1: WQI Parameters and their weight

Parameter	Sn	Recommending Agency for Sn	Computed K	Computer weight (wi) k/Sn
Pb	0.01	WHO	0.00063	0.063
Fe	0.03	WHO	0.00063	0.021
Cd	0.003	WHO	0.00063	0.21
Mn	0.5	WHO	0.00063	0.00126
As	0.01	WHO	0.00063	0.063
Hg	0.001	WHO	0.00063	0.63
Cr	0.05	WHO	0.00063	0.00126

Source field work, 2020

Table 2: Classification of water quality based on weighted arithmetic WQI method

WQI range	Status	Possible usages
0-25	Excellent	Domestic, Irrigation and industrial
26-50	Good	Domestic, Irrigation and industrial
51-70	Average	Irrigation and industrial
71-90	Poor	Irrigation
91-100	Unsuitable for drinking	Restricted to irrigation
>100	Unfit for Drinking	Proper treatment required before use.

Source: Brown et al (1972), Chatterji and Raziuddin (2002)

Results and Discussion

In Tables 3 and 4, it can be seen that values of Lead, Cadmium and Manganese were generally high especially for most areas downstream of the study area, and even higher at the effluent discharge points, and also exceeded the permissible limits for drinking water. Arsenic and mercury values on the other hand were slightly higher that permissible limits for most points in the study area. These findings reflect the observation of Ahmed *et al.,* (2021) that most of these heavy metal pollutants are released by manufacturing, textile, pharmaceutical, paper and fine chemical industries similar to industrial activities in the study area. According to Liu *et al.,* (2014), a number of poorly biodegradable refractory pollutants like petroleum hydrocarbons, sulfides, aniline, naphthalenic acid, organochlorines, olefins, nitrobenzene, alkanes and chloroalkanes, generated by the petrochemical industries are present in wastewater. The composition of petrochemical wastes is chemically very complex and their treatment by biological methods is slow and not very effective (Liu *et al.,* 2014). Even after the primary biological treatment, the organic pollutants are retained in the secondary effluents Ahmed *et al.,* (2021). The standard of Pb for drinking water is 0.05 mg/L; fishing water is 0.05 mg/L; industrial water is 0.01 mg/L; irrigation water is 0.05 mg/L and livestock water is 0.05 mg/L (WHO. 2011, Islam *et al.,* 2015). Above these levels, the water is considered not suitable for drinking or any other activities. Apart from direct ingestion, previous studies have detected heavy metals in the gills, liver, and muscles tissues of various species of fish in contaminated marine ecosystems (Sobhanardakani *et al.,* 2011). Once the heavy metals enter the food chain, they may end up accumulating in the human body (Barakat, 2011). Since most heavy metals are widely applied in industries, exposure and contamination of the workers and residents near such facilities is likely to occur (Kinuthia *et al.,* 2020).

According to the World Health Organization, direct and indirect lead exposure contributes to about 600,000 new cases of children with intellectual disabilities every year (WHO, 2021). Aside from the poisoned futures these children suffer, the economic losses are huge: by lowering the IQ of children, lead exposure costs low- and middle-income countries $977 billion per year (Nestor, 2016). Evidence suggests that Lead may cause fatigue, irritability, information processing difficulties, memory problems, a reduction in sensory and motor reaction times, decision-making impairment, and lapses in concentration (Abadin *et al.,* 1997). In adults, studies have shown that Lead toxicity affects renal system as it causes many effects such as aminoaciduria, glycosuria, and hyperphosphaturia, that is, Fanconi-like syndrome (Kiani and Soltanzadeh 2014). Kidney disease, both acute and chronic nephropathy, is a characteristic of lead toxicity (Abadin *et al.,* 1997). Lead poisoning also inhibits excretion of the waste product urate that causes a tendency for gout, that is, saturnine gout (Agency for Toxic Substances and Disease Registry, 1989, 1997). Dongre, (2020) also reported that Lead inhibits several enzymes required for the synthesis of heme, causing a decrease in blood hemoglobin. Lead interferes with a hormonal form of vitamin D, which affects multiple processes in the body, including cell maturation and skeletal growth Dongre, (2020). Elevated Fe and manganese concentrations on the other hand have been attributed to industrial wastewater. For example Jacukowicz-Sobala *et al.,* (2015) shows that industrial wastes with a high iron or aluminium oxide content are produced in huge quantities as by-products of water treatment (water treatment residuals), bauxite processing (red mud) and hard and brown coal burning in power plants (fly ash). In freshwater, the concentration iron is usually very low with a detection level of 5 μg/L, whereas in groundwater the concentration of dissolved iron is very high with 20 mg/L (EPA, 1993). In countries like Lithuania, many people have been exposed to elevated levels of iron through drinking water, as the collected groundwater exceeded the permissible limit set by the European Union Directive 98/83/EC on the quality of drinking water (Grazuleviciene *et al.,* 2009). The abundance of species such as periphyton, benthic invertebrates and a fish diversity are greatly affected by the direct and indirect effects of iron contamination (Vuori, 1995). The iron precipitate will also cause considerable damage by means of clogging action and hinder the respiration of fishes (EPA, 1993). A study of iron toxicity on aquatic plants, particularly rice, shows that the growth of species of aquatic reed was found to be inhibited by concentration of 1 mg/L total iron (Phippen *et al.,* 2008). Acid soils is known to restrict rice production and together with Zn deficiency cause a macronutrient disorder in wetland rice. The production of lowland rice was greatly affected by high concentrations of reduced iron (Fe^{2+}) in the flooded soils (Becker and Asch, 2005). In another study, Ayers and Westcot (1985), found that high concentration of iron in wastewater contributes to soil acidification and loss of availability of phosphorus and molybdenum when applied to the soil. Thus, iron level in the water samples from River Rido is expected to increase soil acidity and diminish phosphorous in soil when applied.

Cadmium which is also high in River Rido has been recognized for its adverse influence on the enzymatic systems of cells, oxidative stress and for inducing nutritional deficiency in plants (Irfan *et al.,* 2013). Cadmium distributed in the environment will remain in soils and sediments for several decades. Plants gradually take up these metals which get accumulated in them and concentrate along the food chain, reaching ultimately the human body (EPA, 1993; Jaishankar *et al.,* 2014). Cadmium is known to cause both acute and chronic intoxications (Chakraborty *et al.,* 2013). Cadmium is highly toxic to the kidney and it accumulates in the proximal tubular cells in higher concentrations (Jaishankar, *et al.,* 2014). Premature birth and reduced birth weights are the issues that arise if cadmium exposure is high during human pregnancy (Henson and Chedrese, 2004). Chronic toxicity of Cd in children has also been reported to damage of respiratory, renal, skeletal and cardiovascular systems as well as development of cancers of the lungs, kidneys, prostate and stomach (USEPA, 2009, WHO 2011).

Table 3: Mean distribution of sampled heavy metals across sampling points

	Pb (mg/l)	Fe (mg/l)	Cd (mg/l)	Mn (mg/l)	As (mg/l)	Hg (mg/l)	Co (mg/l)	Cr (mg/l)
A (Control)	0.09± 0.001	0.61± 0.005	0.08± 0.0002	0.04± 0.005	0.009± 0.0004	0.008± 0.0004	0.0009± 0.0006	0.005± 0.0004
B	0.17± 0.002	1.28± 0.006	0.48± 0.002	0.92± 0.00004	0.056± 0.001	0.021± 0.0004	0.042± 0.0005	0.0205± 0.0002
C	0.293± 0.0017	1.50± 0.004	0.569± 0.0004	1.162± 0.0005	0.075± 0.011	0.026± 0.0002	0.039± 0.00075	0.022± 0.000005
D	0.416± 0.0031	1.73± 0.004	0.72± 0.0003	1.40± 0.00085	0.083± 0.0006	0.031± 0.00065	0.044± 0.0001	0.031± 0.00045
E	0.392± 0.0019	1.262± 0.0019	0.662± 0.0004	1.002± 0.001	0.078± 0.0003	0.018± 0.0002	0.0324± 0.0003	0.034± 0.00001
F	0.380± 0.0009	0.93± 0.0042	0.502± 0.0065	0.893± 0.0007	0.077± 0.0001	0.0188± 0.0002	0.031± 0.00004	0.0332± 0.00001
G	0.26± 0.0035	0.792± 0.0035	0.321± 0.00075	0.729± 0.00021	0.065± 0.0002	0.013± 0.0004	0.022± 0.0004	0.0286± 0.0003
H	0.264± 0.0063	0.62± 0.0052	0.311± 0.0006	0.690± 0.00046	0.043± 0.0002	0.013± 0.00001	0.023± 0.00045	0.027± 0.00025
I	0.235± 0.0035	0.443± 0.00005	0.288± 0.0003	0.642± 0.00056	0.043± 0.00055	0.0091± 0.00035	0.0197± 0.00026	0.0207± 0.00004
J	0.141± 0.0019	0.4185± 0.00046	0.276± 0.00022	0.532± 0.00005	0.038± 0.0006	0.009± 0.00035	0.0121± 0.00037	0.0193± 0.00005
K	0.141± 0.0047	0.296± 0.0006	0.186± 0.0005	0.332± 0.0004	0.0402± 0.0004	0.01± 0.00056	0.0967± 0.0004	0.01943± 0.00025
WHO MPL	0.01	0.03	0.003	0.50	0.01	0.001	NA	0.05
NSDWQ MPL	0.01	0.03	0.003	0.20	0.01	0.001	NA	0.05

B: Northern noodles effluent discharge point; C: Refinery effluent discharge point; D-K Locations Downstream

Arsenic, and mercury have also been reported in industrial wastewater, all of which have implications for human health and the environment (Lambert *et al.,* 2000). Arsenic is one of the most important heavy metals causing disquiet from both ecological and individual health standpoints (Hughes *et al.,* 1988). Arsenic has a semimetallic property, is prominently toxic and carcinogenic, and is extensively available in the form of oxides or sulfides or as a salt of iron, sodium, calcium, copper, etc (Singh, *et al.,* 2007). Humans are exposed to arsenic by means of air, food and water (Jaishankar *et al.,* 2014). Drinking water contaminated with arsenic is one of the major causes for arsenic toxicity in more than 30 countries in the world (Chowdhury et al., 2000). If the arsenic level in ground water is 10–100 times the value given in the WHO guideline for drinking water (10 µg/L), it can be a threat to human health (Hoque *et al.,* 2011). Water may get contaminated through improperly disposed arsenical chemicals, arsenical pesticides or by natural mineral deposits (WHO, 2011). Long-term exposure to arsenic is known to lead to the formation of skin lesions, internal cancers, neurological problems, pulmonary disease, peripheral vascular disease, hypertension and cardiovascular disease and diabetes mellitus (Smith *et al.,* 2000). Chronic arsenicosis results in many irreversible changes in the vital organs and the mortality rate is higher. Major sources of mercury pollution include anthropogenic activities such as agriculture, municipal wastewater discharges, mining, incineration, and discharges of industrial wastewater (Chen *et al.,* 2012). Mercury is very toxic and exceedingly bioaccumulative (Butu *et al.,* 2019). Its presence adversely affects the marine environment and hence many studies are directed towards the distribution of mercury in water environment (Jaishankar *et al.,* 2014). Exposure to elevated levels of metallic, organic and inorganic mercury can damage the brain, kidneys and the developing fetus (Alina *et al.,* 2012). Organic mercury can easily permeate across the biomembranes and since they are lipophilic in nature, mercury is present in higher concentrations in most species of fatty fish and in the liver of lean fish (Reilly, 2007). Due to the excess health effects associated with exposure to mercury, the present standard for drinking water has been set at lower levels of 0.002 mg/L and 0.001 mg/L by the Environmental Protection Act and World Health Organization (WHO, 2004).

In Table 4, result of comparison test shows significant difference in the levels of heavy metal concentration between effluent discharge points and control point as well as between control point and points downstream of the study area (Table 6), an indication of increased concentrations at effluent discharge point and areas downstream of the study area as against control point. In Table 5, however, significant difference was not detected in the concentration levels between the points discharge and areas downstream of the study area. The above results are an indication of pollution at discharge point and points downstream of the study area. To buttress the above findings, Tables 9 and 10 revealed significant differences in the levels of heavy metals between discharge points, points downstream of the study area and the permissible limits for drinking water as stipulated by WHO (2011). In Tables 11 and 12, results of water quality index of heavy metals at effluent discharge points and points downstream of the study area showed that River Rido is highly contaminated and unfit for consumption. According to Saleem *et al.*, (2015), heavy metal concentrations determined in water and sediment can be used to evaluate the anthropogenic and industrial impacts and risks caused by wastewater discharges in the rivers. Existing studies indicates that heavy metal pollution in surface waters is generally implicated in areas where the industry is developed and the population is very high (Bhardwaj *et al.*, 2017; Vu *et al.*, 2017; Sarah *et al.*, 2019).

This is the case with the study area which is characterised by high population coupled with industrial activities. Heavy metals cause severe problem for humans and aquatic ecosystems if discharged in water through industries and other sources due to particular toxic, hazardous, and carcinogenic nature as well as accumulations in the body based on relative chemical and physiological characteristics (Baghel and Singh, 2016; Dongre and Gedam, 2019). Study has further shown that grading water quality indicators largely depends on indicator concentration and the rate of relative toxicity (Withanachchi *et al.*, 2018). One of the most applicable methods is Water Quality Index (WQI) that summarizes the quality of water for drinking and other purposes (Belkhiri, *et al.*, 2018; Liang, *et al.*, 2018; Reyes-Toscano, *et al.*, 2020). This index provides a single number as a measure of overall water quality at a specific location and time (Liang, *et al.*, 2018). Studies which have also adopted the water quality index with regards to heavy metals include Sahoo *et al.*, (2020); Chaturvedi *et al.*, (2019); Chaturvedi *et al.*,(2018); Azizi, and Mohammadzadeh (2012).

Table 4: Students'-t test for difference in heavy metal levels between mean effluent discharge points and control point

	Pb (mg/l)	**Fe (mg/l)**	**Cd (mg/l)**	**Mn (mg/l)**	**As (mg/l)**	**Hg (mg/l)**	**Co (mg/l)**	**Cr (mg/l)**	*P-value 0.05 T test*
Mean Effluent Discharge Points	0.228	1.395	0.525	1.039	0.070	0.024	0.041	0.021	*0.028*
Mean Control point	0.091	0.605	0.078	0.041	0.009	0.008	0.009	0.005	

Difference statistically significant at 0.05 level of confidence

Table 5: Students'-test for difference in Heavy Metal levels between Mean effluent discharge points and downstream points

	Pb (mg/l)	**Fe (mg/l)**	**Cd (mg/l)**	**Mn (mg/l)**	**As (mg/l)**	**Hg (mg/l)**	**Co (mg/l)**	**Cr (mg/l)**	*P-value 0.05 T test*
Mean Effluent Discharge Points	0.228	1.395	0.525	1.039	0.070	0.024	0.041	0.021	*0.079*
Mean downstream Points (D-K)	0.279	0.811	0.041	0.778	0.058	0.152	0.024	0.027	

Difference is not statistically significant at 0.05 level of confidence

Table 6: Students'-test for difference in mean heavy metal levels between control point and downstream

	Pb (mg/l)	**Fe (mg/l)**	**Cd (mg/l)**	**Mn (mg/l)**	**As (mg/l)**	**Hg (mg/l)**	**Co (mg/l)**	**Cr (mg/l)**	*P-value 0.05 T test*
Mean Control point	0.091	0.605	0.078	0.041	0.009	0.008	0.009	0.005	*0.031*
Mean Downstream Points (D-K)	0.279	0.811	0.041	0.778	0.058	0.152	0.024	0.027	

Difference statistically significant at 0.05 level of confidence

Table 7: Descriptive statistics of mean heavy metals at Effluent discharge points (northern noodles & refinery)

	Mean	SE	Variance	Range	Min	Max	Sum	Count	Cong. Level
Pb (mg/l)	0.228± 0.069	0.028	0.0048	0.132	0.162	0.294	1.37	6	0.073
Fe (mg/l)	1.395±0.1200	0.049	0.0144	0.227	1.28	1.51	8.36	6	0.125
Cd (mg/l)	0.525±0.048	0.0196	0.0023	0.0898	0.48	0.569	3.15	6	0.0505
Mn (mg/l)	0.070±0.008	0.0548	0.018	0.245	0.916	1.162	6.34	6	0.1409
As (mg/l)	0.0701±0.0084	0.0035	0.00007	0.0194	0.062	0.081	0.421	6	0.0089
Hg (mg/l)	0.0239±0.003	0.0013	0.0007	0.0064	0.021	0.027	0.143	6	0.0033
Co (mg/l)	0.0409±0.0013	0.00053	0.00007	0.003	0.039	0.043	0.245	6	0.00137
Cr (mg/l)	0.021±0.0005	0.00024	0.00003	0.0013	0.0203	0.022	0.126	6	0.00063

Source: field work 2020

Table 8: Descriptive statistics of mean heavy metals at downstream points (D-K)

	Mean	SE	Variance	Range	Min	Max	Sum	Count	Cong. Level
Pb	0.279±0.104	0.021	0.0107	0.282	0.136	0.418	6.706	24	0.043
Fe	0.811±0.464	0.095	0.216	1.437	0.295	1.732	19.46	24	0.196
Cd	0.408±0.187	0.0382	0.0350	0.535	0.186	0.720	9.80	24	0.079
Mn	0.778±0.311	0.063	0.096	1.070	0.33	1.40	18.67	24	0.131
As	0.058±0.0183	0.0037	0.0004	0.045	0.0382	0.083	1.397	24	0.0077
Hg	0.0152±0.0071	0.0014	0.00005	0.023	0.0087	0.032	0.365	24	0.0029
Co	0.024±0.011	0.0022	0.0001	0.035	0.0093	0.044	0.585	24	0.0046
Cr	0.0268±0.0059	0.00121	0.0005	0.015	0.019	0.034	0.64	24	0.0025

Source: field work 2020

Table 9: Students'-test for difference in Heavy Metal levels between Mean effluent discharge points and WHO Standards

	Pb (mg/l)	**Fe (mg/l)**	**Cd (mg/l)**	**Mn (mg/l)**	**As (mg/l)**	**Hg (mg/l)**	**Co (mg/l)**	**Cr (mg/l)**	*P-value 0.05 T test*
Mean Effluent Discharge Points	0.228	1.395	0.525	1.039	0.070	0.024	0.041	0.021	*0.038*
WHO PML For drinking water	0.01	0.03	0.003	0.50	0.01	0.001	0.0001	00.50	

Difference is statistically significant at 0.05 level of confidence

Table 10: Students'-test for difference in Heavy Metal levels between Mean downstream points and WHO Standards

	Pb (mg/l)	**Fe (mg/l)**	**Cd (mg/l)**	**Mn (mg/l)**	**As (mg/l)**	**Hg (mg/l)**	**Co (mg/l)**	**Cr (mg/l)**	*P-value 0.05 T test*
Mean Downstream Points	0.279	0.811	0.041	0.778	0.058	0.152	0.024	0.027	*0.026*
WHO PML For drinking water	0.01	0.03	0.003	0.50	0.01	0.001	0.0001	00.50	

Difference is statistically significant at 0.05 level of confidence

Table 11: Water Quality Index (WQI) of heavy metals at effluent discharge points in River Rido

Parameter	Observed values (vi)	Standard values (si)	Unit weights (wi)	Quality rating (qi)	$wiqi$	Interpretation
Pb mg/I	0.228	0.01	0.063	2280	143.6	Unfit for Drinking
Fe mg/l	1.39	0.03	0.021	4630	97.23	Unfit for Drinking
Cd mg/I	0.53	0.003	0.21	17660	3708.6	Unfit for Drinking
Mn mg/I	0.07	0.5	0.00126	14	0.018	Unfit for Drinking
As mg/l	0.02	0.01	0.063	200	12.6	Unfit for Drinking
Hg mg/l	0.04	0.001	0.63	4000	2520	Unfit for Drinking
Cr mg/l	0.021	0.05	0.00126	42	0.053	Unfit for Drinking
					$\sum_{i=1}^{n} w_i - q_i = 926.0$	

Table 12: Water Quality Index (WQI) of heavy metals at downstream points in River Rido (D-K)

Parameter	Observed values (vi)	Standard values (si)	Unit weights (wi)	Quality rating (qi)	$wiqi$	Interpretation
Pb mg/I	0.28	Standard values (si)	Unit weights (wi)	2800	176.4	Unfit for Drinking
Fe mg/l	0.81	0.01	0.063	2700	56.7	Unfit for Drinking
Cd mg/I	0.78	0.03	0.021	26000	5460	Unfit for Drinking
Mn mg/I	0.058	0.003	0.21	11.6	0.015	Unfit for Drinking
As mg/l	0.12	0.5	0.00126	1200	75.6	Unfit for Drinking
Hg mg/l	0.02	0.01	0.063	2000	1260	Unfit for Drinking
Cr mg/l	0.027	0.001	0.63	54	0.068	Unfit for Drinking
					$\sum_{i=1}^{n} w_i - q_i = 1004.1$	

Conclusion and Recommendations

In this study, the effects of effluents from Northern Noodles discharge and NNPC Refinery on the levels of heavy metals in River Rido in Kaduna State was investigated. This study showed that water samples from River Rido is contaminated by heavy metals. Of the metals investigated, the mean concentration of Pb, Fe, Cd, As, Mn and Hg were relatively higher than those of Co and Cr in the samples analyzed. The levels of Pb, Fe, and Cd in water samples were generally higher than the allowable limits set by WHO, NSDWQ, hence becoming a public health concern. Levels of heavy metals at control point were also lower than levels found at locations downstream of the study area and at the effluent discharge points. This was an evidence of a build-up of toxic metals in the water. Presence of residential areas downstream of the study area could also have been a pathway through which the metallic contaminants could eventually find their way into the water body. Therefore, there is need to formulate and adopt policies that would translate to sustainable wastewater management and treatment infrastructure in order to minimize the environmental health hazards associated with effluent discharge in the study area. Furthermore, residents living around the study area who reply on the river for domestic purposes should be made aware of the health hazards that could emanate from exposure to untreated wastewater through public education and awareness campaigns. Finally, regular monitoring of pathways to exposure and probable intervention for reducing additional exposure to heavy metals in the study area can become a germane step towards prevention.

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