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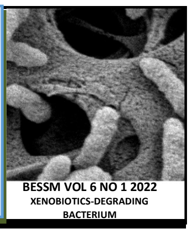

Effects of Refining and Petrochemical Effluents on Water Quality and Zooplankton Community in River Rido Kaduna, Nigeria

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ABSTRACT

Kaduna Refining and Petrochemical Corporations (KRPC) discharges were studied for a year along the river Rido to determine their impact on water quality and the distribution and abundance of Zooplankton. Physical and chemical parameters were measured following American Public Health Association (APHA) standards for evaluating wastewater. An atomic absorption spectrometer (AAS) was utilized for heavy metal analysis. For this experiment, we used a Plankton net with a 25 µm mesh size and a specimen bottle with a 10 cm diameter ring opening to collect zooplankton. Zooplanktons were identified using a standard key and a monograph. Water quality parameters fluctuated, but all were within acceptable ranges except for temperature, conductivity, Total Dissolved Solid, and lead. Zooplanktons were represented in order of abundance by 8 species of protozoa constituting 72.44%, followed by 12 species of Rotifera (10.58%), followed by 13 species of Cladocera 9.55% and then 6 species of Copepoda (7.44%). The planktons showed seasonal variation with high density recorded during the wet season in all the stations. There was a low density of zooplankton in station B, while high density was observed in stations A and D. Also, the low transparency and dissolved oxygen (DO) as well as high mean values of temperature (30.88 °C), chloride (31.88 mg/L), lead (0.099 mg/L), TDS (224.17 mg/L) and conductivity (334.28 µS/cm) observed were above FEPA limits at station B were an indication of pollution and deterioration of water quality. This research revealed that the effluent discharge from KRPC has adverse effects on the zooplankton community and the water quality of river Rido.

INTRODUCTION

Degradation of the natural environment is a major problem in many places, especially in developing countries, and one of the main causes of this problem is the discharge of industrial effluent into water bodies [1,2]. When humans introduce harmful substances or energy into the aquatic environment, it can have negative consequences for aquatic life, human health, recreational activities like fishing, water quality, and the value of the surrounding land [3]. Freshwater sources like rivers and lakes are vital for agriculture, manufacturing, and human consumption. This ranges from simple necessities like drinking and cooking water to more complex uses in industries like tourism and agriculture. The aquatic biota is under stress because rivers, lakes, streams, ponds, the sea, and the ocean are polluted beyond their carrying capacities [4]. Some species of organisms may go extinct while others may thrive as a result of shifts in the physicochemical parameters of water bodies, which can affect their survival, growth, and reproduction [5].

Zooplanktons are microscopic animals found in the aquatic ecosystem. They are heterotrophic planktonic animals floating in water [6], and depend on the phytoplankton for their dissolved or particulate foodstuffs [7]. Adults (holoplankton) or their offspring (eggs and larvae) can be found in the pelagic environment, and they represent nearly every animal taxon (meroplankton). Zooplankton is a major link in the secondary level of energy transfer in aquatic food webs between autotrophs

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and heterotrophs, making it one of the most important biotic components in ecology [8]. They are the primary food source for higher animals such as fishes, especially fish larvae, and they get their nutrition from phytoplankton. Microscopic Protozoan, Rotifers, two subclasses of the Crustacea; Cladocerans and Copepods, are the most common and dominant zooplankton in freshwaters [9]. Because of their strong sensitivity to environmental conditions and rapid response to changes in environmental quality, zooplankton is useful indicators of water quality. They affect all the functional aspects of an aquatic ecosystem, including food chains, food webs, energy flow, and the cycling of matter [10,11].

In particular, refinery effluents containing petroleum components like aliphatic hydrocarbons, heavy metals, and polycyclic aromatic hydrocarbons have been deemed harmful to public health (PAH) [2,12,13]. Fish and aquatic life were reported to be missing at the site of the Warri Refinery and Petrochemical Company's (WRPC) effluent discharge and all downstream sites leading to the Ubeji River [14]. Compared to downstream locations along the river Rido, the effluent from Kaduna Refining and Petrochemical Company has been shown to reduce chlorophyll and gross primary productivity [15]. [1] reported that contaminants from the effluent discharge caused the river Romi's physicochemical parameters to rise above the acceptable limit set by National Standard, Nigeria and the World Health Organization. Researchers discovered that river pollution slows down natural water purification processes and reduces the rate at which plants can produce oxygen through photosynthesis.

Based on the reported incidences and other related studies it was agreed that petroleum refinery effluents posed serious adverse effects to both aquatic and human life in the environment and particular aquatic ecosystem, it, therefore, becomes indispensable to assess the effects of Kaduna refining and petrochemical effluent on the abundance and distribution of plankton community in river Rido, Kaduna state, Nigeria, to contribute to knowledge on the current condition of plankton diversity in the river for conservation of biodiversity and environmental monitoring. Therefore, monitoring and assessment of the aquatic ecosystem for any disturbances which may result to change in the community structure of aquatic biota and impairment of the water quality are necessary for conserving biodiversity and sustainability of natural resources in our environment. The present research aimed at determining the effects of refining and petrochemical effluents on water quality and the zooplankton community of river Rido Kaduna Nigeria.

MATERIALS AND METHODS

Study area

The research took place along the river Rido in Chikun Local Government Area, on the southwestern outskirts of Kaduna metropolis, Kaduna state, North-Western Nigeria. Situated at 100°35′N and 070°28′E, it is relatively close to the equator. There are two (2) distinct seasons in the state of Kaduna: the dry season and the wet season. It is believed that the 16-kilometer-long River Rido begins in Kujama. Many neighbourhoods are crossed by this waterway before it reaches the Kaduna Refining and Petrochemical Corporation and the river. The lives of the locals in the area, and the Kaduna people more broadly, are profoundly affected. Drinking, irrigation, fishing, laundering, bathing, transportation, and industrial uses are just a few of the many areas that are affected.

Sampling sites

In this investigation, we chose to sample from four (4) different locations (A-D). Station A can be found upstream of the river, past Rido town, and before Kaduna Refining and Petrochemicals Corporation. When the effluent from the Kaduna Refining and Petrochemical Complex is released into the River Rido, it does so at Station B. Approximately 2 kilometres downstream from the effluent discharge point at Kaduna Refining and Petrochemical Cooperation is where you'll find Station C. Currently, the water is shallow, wide open, and moving quickly. Comparatively, Station D is situated four kilometres downstream from the river, or four kilometres further from the effluent discharge point. It's open, deep, and moving very slowly.

Water sampling

Samples for Physico-chemical parameters analysis were collected between 8-11a.m at each sampling station monthly for 12 months (one year). Clean jerry cans were used to collect a water sample from the river. A jerry can be lowered into the river and a water sample was collected from the subsurface water. Water samples for the analysis of trace metals were also collected in glass bottles. Water samples were labelled, placed in plastic containers, and transported to the Biological Science Department Laboratory at the Nigerian Defense Academy (NDA) in Kaduna for physicochemical parameter analysis following [16] and American Public Health Association [17] guidelines.

Determination of Physicochemical parameters and heavy metals

Standard procedures for wastewater assessment were followed in order to establish physicochemical parameters [17,18]. pH and Temperature were measured with a Microcomputer pH meter (HI8424 HANNA instrument). A strong, tautly attached heavy weight, was lowered into the water to gauge its depth. Using a Secchi disc, we measured the clarity of the water. The PHOX 52 combined Conductivity and Total Dissolved Solid (TDS) meter were used to measure these parameters at sampling sites, while the Dissolved Oxygen (DO) and Biochemical Oxygen Demand (BOD) levels were measured by a Jenway 970 Model waterproof DO meter. Sulphate, nitrite, phosphorus, chloride, magnesium, oil, and grease concentrations were all measured with a HACH spectrophotometer (model DR2010).

The chemical oxygen demand (COD) was measured by placing 50 mL of the sample water into a reflux flask and subjecting it to a process of digestion and titration. To make the solution more stable, 1g of mercuric sulphate (Ag_2SO_4) was added. A further 5 mL of concentrated sulphuric acid (H_2SO_4) was added to the mixture. As 25 mL of 0.25N Potassium dichromate solution and sulphuric acid were added, the solution was slowly swirled to facilitate complete dissolution of the Ag_2SO_4. For an hour, the mixture was allowed to slowly bubble away. After it cooled down, it was mixed with water. It took about three or four drops of the Ferroin indicator to achieve the desired colour, and the solution was titrated against 0.1N of Ferrous Ammonium Sulphate (FAS). The volume of the FAS was measured, and a sudden transformation from blue-green to reddish brown indicated the end of the process. Heavy metals including copper, zinc, lead, arsenic, cadmium, nickel, copper, and iron, were determined, after NHO_3 digestion of the sample, using Atomic Absorption Spectrophotometer (AAS), following standard procedure [17].

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Plankton sampling

Samples of zooplankton were gathered using a Plankton net with a 25 mm mesh size that was fastened to the base of a specimen bottle with a 10 cm diameter ring opening. At each sampling location, 100 litres of water were filtered through the plankton net to collect a sample of plankton for counting purposes. To collect plankton samples, one hundred litres of water was filtered through a plankton net suspended above the river's surface and used to collect water from the euphotic zone. About two or three drops of formaldehyde at 4% were used to preserve the samples [5,9,19].

Sedimentation

The plankton samples were brought back to the lab and placed in test tubes for sedimentation. All of the labelled test tubes were placed on a rack and covered with a cover slip. The rack was stored in the dark cupboard for a period of 24 to 48 hours on a vibration-free surface. Then, the concentrated plankton samples were moved from the test tube to the 10 mL specimen bottle by removing the supernatant. This plankton sample was suspended in distilled water to a final volume of 10 mL [19].

Identification of planktons

The fixed plankton samples were allowed to settle in the laboratory for 24hrs-48hrs. After settling, the supernatant was decanted and allowed the sediment. The plankton sample was collected with the aid of a 1-mL dropping pipette and a drop was placed on a glass slide and covered with a cover slip. A low and high-power compound microscope (Olympus Japan) was used for microscopic viewing of planktons. The prepared slides were separately mounted on the microscope stage and viewed using 10X, 40X, 100X and 200X magnifications. Standard keys and monographs; [20,21], were used for the identification of the planktons.

RESULTS

Physico-chemical parameters in river Rido

The average values of physicochemical parameters measured at Rido river stations A, B, C, and D are listed in **Table 1**. It was found that the average depth varied greatly between the two stations, with 81.07 cm being recorded at station A and only 39.78cm being recorded at station B. Station B had the highest average temperature at 30.880 degrees Celsius, while station A had the lowest average temperature at 24.120 degrees Celsius. All stations' temperatures fell within the safe range specified by [22,23]. Overall, the pH values were relatively consistent across the stations, with a range of 7.19 at station C to 7.74 at station D. While the mean value of dissolved oxygen (DO) was highest at station A (6.21 mg/L), it was lowest at station B (4.77 mg/L) and well within the FEPA and WHO guidelines for acceptable levels of DO.

Biochemical oxygen demand (BOD) averaged 3.01 mg/L at station A and 3.77 mg/L at station C, with no discernible difference between the study sites. Chemical Oxygen Demand (COD) values were extremely low across the board, with station D having the lowest at 0.02 mg/L and station A having the highest at 0.314 mg/L. For Alkalinity, the highest average was recorded at Station B (40.29 mg/L), while the lowest was recorded at Station A (24.921 mg/L). Station A had TDS values of 43.75mg/L, while station B had TDS values of 224.17 mg/L.

While station A recorded the lowest mean conductivity (63.08 mg/L), station B recorded the highest (334.5 mg/L), which is well above the limits set by the FEPA and the WHO. Station A had the highest average transparency (30.08 cm), while station B had the lowest (12 cm). Station B had the highest average sulphate concentration (41.92 mg/L), while station A had the lowest average (8.78 mg/L). Nitrite concentrations were found to be on average 0.065 mg/L at station C and 0.123 mg/L at station B. Magnesium's mean value (205.02 mg/L) was highest in station D, exceeding both the FEPA and WHO guidelines for safety, and the lowest in station B (143.02 mg/L). Phosphate mean values were found to vary between 13.15 and 17.28 mg/L between stations B and A, respectively. The average was 31.88mg/L at station B and 13.78mg/L at station A. In station A, oil and grease concentrations were measured at 0.964 mg/L, while in station B, they were measured at 1.83 mg/L. All the mean values were above the permissible limits of FEPA (0.05mg/L), except for station A, which had the lowest concentration (0.041 mg/L), and lead showed a gradient decrease downstream in the river. Nickel, copper, zinc, and iron all had statistically insignificant mean values across all of the study sites. All the same, station B's measurements of temperature, conductivity, Total Dissolved Solid, and Lead were too high to be considered safe by the FEPA and WHO (**Table 1**).

Table 1. Mean values of physico-chemical parameters and heavy metals from River Rido Kaduna.

Parameters	Stations				FEPA*	WHO**
	A	B	C	D		
Depth (cm)	81.07	39.78	74.83	75.54	NS	NS
Temperature °C	24.22	30.88	25.58	26.00	30	30
pH	7.22	7.29	7.19	7.74	6.5-8.5	6.5-8.5
D.O (mg/L)	6.21	4.77	5.98	5.38	10	10
BOD (mg/L)	3.01	3.38	3.77	3.57	10	10
COD (mg/L)	0.03	0.02	0.025	0.02	40	40
Alkalinity (mg/L)	24.92	40.29	29.54	30.71	NS	600
TDS (mg/L)	43.75	224.17	108.42	120.58	200	250
Conductivity (μS/cm)	63.08	334.50	155.75	172.25	240	250
Transparency (cm)	30.28	12.00	26.09	26.47	NS	NS
Sulphate (mg/L)	8.78	41.92	23.33	17.33	500	400
Nitrite (mg/L)	0.113	0.128	0.06	0.08	NS	NS
Magnesium (mg/L)	165.92	143.02	196.66	205.23	200	150
Phosphate (mg/L)	17.28	13.15	14.18	15.65	5	10
Chloride (mg/L)	12.78	31.88	14.99	16.47	200	250
Oil & Grease (mg/L)	0.964	1.83	1.25	1.59	10	NS
Lead Pb (mg/L)	0.041	0.099	0.078	0.068	0.05	<1
Nickel Ni (mg/L)	0.117	0.096	0.120	0.127	<1	<1
Copper Cu (mg/L)	0.020	0.026	0.023	0.0087	1.5	<1
Zinc Zn (mg/L)	0.009	0.009	0.010	0.0089	1	<1
Iron Fe (mg/L)	0.118	0.067	0.088	0.105	1	1

*FEPA (1991): Federal Environmental Protection Agency effluent Standards
**WHO (1984): World Health Organisation guidelines for drinking water
NS= Not Specified

Distribution and composition of Zooplankton species in river Rido

The results of zooplankton species identified in river Rido are presented in **Table 2**. The results indicated a total number of 34 species of zooplankton were identified throughout the period of the study. Cladoceran had the highest number of individual species (11), followed by Rotifers which were represented by ten (10) species. Protozoa and Copepoda were represented by eight (8) and five (5) species respectively.

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Table 2. The zooplankton species identified in River Rido.

Major classes	Protozoa	Rotifera	Cladoceran	Copepoda
Zooplankton species	*Amoeba proteaus*	*Anapus* spp.	*Acroperus harper*	*Diaptomus* spp.
	Arcella vulgaris	*Brachionus* spp.	*Alona quadrangularis*	*Eucyclops* spp.
	Centrpyxis arculeata	*Diastyla* spp.	*Alona* spp.	*Mesocyclops* spp.
	Difflugia pyriformis	*Euchlanis* spp.	*Bosmina longirostris*	*Nauplias* spp.
	Euglypha ciliate	*Gastropus*	*Ceriodaphnia* spp.	*Tropocyclops* spp.
	Nebella colaris	*Habratrocha*	*Chydorus sphearicus*	
	Paramecium spp.	*Monostyla lecene*	*Daphnia* spp.	
	Trinema enchelyx	*Pleurosoma* spp.	*Diaphanosoma* spp.	
		Philodina spp.	*Pleuroxus striatus*	
		Testudinella patina	*Pricripleurxus denticulatus*	
		Trichocerca spp.	*Pseudochydorous globosus*	

Relative abundance and of zooplankton divisions in River Rido

Fig. 1 shows zooplankton abundance and distribution in the study stations of river Rido. Protozoa were dominant among the zooplankton divisions in all the four stations followed by Rotifers in station A, Cladocerance in stations B and C, and Copepods in station D. The least in abundance was Copepods in station A and C, Rotifers in station B and Cladocerans in station D. There was no significant difference between zooplankton groups in all the stations.

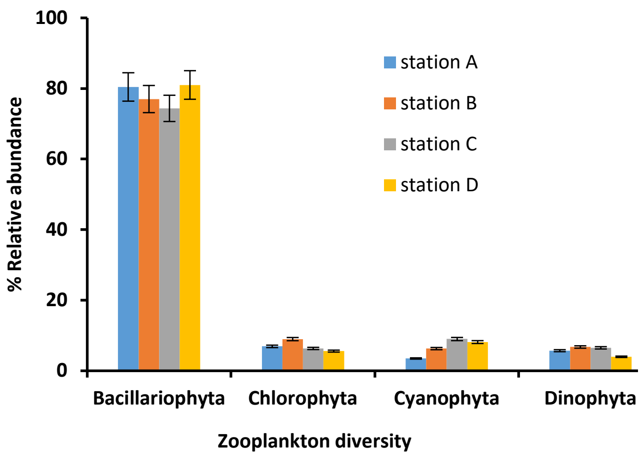

Fig. 1. The relative abundance of zooplankton divisions in River Rido.

DISCUSSION

In station B, where a higher load of organic matter was found in the effluent, a lower mean value of DO was obtained. Having a low dissolved oxygen concentration can be deadly for fish and other aquatic organisms because it disrupts their normal bodily processes [2]. Phosphate levels that are too high (above FEPA and WHO guidelines) can cause eutrophication, which in turn can cause high primary productivity but then lead to algal bloom and poor water quality. This will lead to a decline in water quality and, ultimately, fish deaths [3,24]. It is clear that the effluents have manifested in the aquatic environment, as evidenced by the high lead values recorded at all stations apart from station A-the control point, with the highest concentration recorded value obtained at the point of effluent discharge from the Refinery. Lead is persistent in the environment, and it can bioaccumulate and magnify in the food chain to reach not only higher aquatic organisms like fish, but also humans, who can get the highest dose by directly ingesting the water and consuming the fish. Conductivity and magnesium measurements taken at stations B and D showed a high presence of dissolved ions in the water, which could have come from the effluent discharge point or the farmland along the riverbank. These measurements exceeded the Federal Environmental Protection Agency and the World Health Organization's recommended limits.

Numerous studies on the abundance and distribution of zooplankton in Nigerian freshwater have confirmed the following order of abundance: Protozoan > Rotifer > Copepod > Cladocera [25]. [26] emphasized that protozoa, with their rapid reproduction rates, made up the bulk of the zooplankton assemblage. Pollution has diminished the physical and chemical properties of the living environment, which may explain why there aren't more Copepods and Cladocerans [25]. The relative ecological interaction and inter-relationship between the biotic and abiotic components of the aquatic ecosystem were attributed to the significant association observed between the abundance and distribution of zooplanktons and some of the Physico-chemical parameters at the four (A, B, C, and D) different stations in river rido. Intensified nutrient availability led to a rise in plankton numbers. Consequently, the high density of planktons in station A is a direct result of the positive relationship between these variables, while the low density of planktons in station B is an indirect result of the inverse relationship between Magnesium and chloride. The negative correlation with magnesium indicated high nutrient uptake at low concentrations, suggesting that low DO may be caused by nutrients in the water [27].

The positive correlation between Protozoan and temperature in station 'A' could be because the temperature was not beyond the optimal level and therefore favourable for the growth and survival of the plankton. But the positive correlation observed with pH and nitrite in station B indicated high nutrient loading and alkaline pH and influenced high phytoplankton production which supported the zooplankton population and thus favoured the growth and increase of the protozoan [28]. Higher values of temperature, conductivity, TDS, and sulphate (above the permissible limit by FEPA and WHO), chloride, oil, and grease, and lower values of dissolved oxygen, transparency, and phosphate recorded at station B indicated that the effluent significantly contributed to pollutants loading, which induced alteration and impairment of the physicochemical properties and consequently deleterious effects on the planktonic community [27].

The variations that occurred among the physicochemical parameters at different stations in river Rido suggested that each station has its structure in terms of the physical, chemical and biological components. The presence of suspended particles and the shallowness of the river at station B likely contributed to the high temperatures, total dissolved solids, conductivity, and chloride concentrations measured there. However, it was observed that as the distance downstream from the effluent entry point increased, the river diluted and self-purified itself, creating favourable physicochemical conditions for the growth and increase of plankton. The influence of seasons was shown in the variability in physical-chemical parameters fluctuating between wet and dry seasons which had significant ecological implications on the community structure and abundance of planktons. The significant high quantity of DO during the wet season compared to the dry season in station A indicates high photosynthetic activities, since the major part of dissolved

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oxygen is observed to come from photosynthesis [29]. Only small parts come from the atmosphere. [30] reported that eutrophic, productive water bodies tend to have higher concentrations of dissolved oxygen. High transparency during the dry season at stations A and D may be the result of a combination of factors, including a decrease in the number of suspended substances and allochtonous substances that enter the water during floods and the presence of fewer dissolved solids (TDS) and suspended particles that interfere with light intensity [31]. Also, low water turbulence and velocity could result in high transparency of the water during the dry season.

The high concentration of chloride during the dry season in stations C and D could be a result of concentration due to water evaporation and a low volume of water. it has been reported that eutrophic and productive water bodies are typically associated with rising dissolved oxygen levels in aquatic systems. Stations A and D's high transparency during the dry season may be attributable to a combination of factors, including low total dissolved solids (TDS) and suspended particles that interfere with light intensity, and a decrease in TDS and allochthonous substances that enter the water during the wet season [32]. The high magnesium concentration during the wet season in station C could be a result of high nutrient availability which favoured plankton growth. While the low concentration of phosphate indicated high uptake by abundant phytoplankton which is an indication of high primary productivity. Low phosphate availability is one of the many factors that reduce primary productivity in freshwater ecosystems. Low decomposition activities by aerobic microorganisms and low oxygen uptake through respiration may explain the high quantity of DO seen during the dry season at station D.

The seasonal and spatial variability observed in the distribution and abundance of zooplanktons, and physicochemical parameters at the four (A, B, C and D) different stations in river Rido showed that there was a significant interplay between abiotic and biotic ecological factors at the respective stations in the river. The relatively low density of the planktons recorded at station B which is near the point of entry of Kaduna Refining and Petrochemical effluent may not be unconnected with the impacts of the contaminants received in the effluent. It has been pointed out by [33] and that the various seasonal biological rhythms are controlled in large part by physicochemical factors. Plankton populations were reduced by unfavourable physicochemical conditions, while those were boosted by more ideal water conditions. The life processes of planktonic populations are affected by the inflow of sewage and the decomposition of waste materials in the catchments area, and these populations show a response to seasonal parameters such as temperature, dissolved oxygen, pH, and nutrient concentration of the medium [29].

CONCLUSION

This research revealed the significant difference in some of the physicochemical parameters such as depths and transparency observed among the stations, as well as temperature, TDS, conductivity, and chloride, particularly between station A (control) and station B (effluent discharge point) with the highest values, indicated adverse effects of Kaduna Refinery and petrochemical effluent in the water, particularly around the point of discharge. Although the differences in the abundance and distribution of zooplankton species were not statistically significant, the relatively high abundance and distribution of the species in station A has shown the extent of the effects of effluent in river Rido, particularly at station B which has the lowest density of the planktonic species observed in this research. Both linear and inverse associations were observed between Physico-chemical parameters and plankton species distribution and abundance at different study stations.

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