Downstream Effects of Industrial Effluents Discharge on Some Physicochemical Parameters and Water Quality Index of River Rido, Kaduna State, Nigeria

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ABSTRACT: The effects of industrial effluent discharge on the water quality of River Rido in Kaduna South, Kaduna State, were examined. These include the Northern Noodles discharge point, the Kaduna Refinery discharge point, and points downstream of the River Rido. An interval of 100m between sampling points was established to achieve an even representation of sampling points. The physico-chemical parameters investigated include pH, free dissolved carbon dioxide, alkalinity, hardness, sodium, electrical conductivity, Turbidity, total suspended solids, total phosphate, nitrate, sulfate, and dissolved oxygen. Mean levels of turbidity Total suspended solids and total phosphate at effluent discharge points, as well as in most areas downstream of the study area, were generally above permissible limits for drinking water. Statistical differences were observed in the concentration levels of investigated parameters between the control point and effluent discharge points, as well as between the control point and areas downstream of the study area. However, concentration levels were observed to be similar between discharge points and areas downstream of the study area, an indication of contamination downstream by effluent discharge upstream. Notwithstanding, the water quality index of physico-chemical parameters at both effluent discharge points and areas downstream of River Rido shows that the quality of the river ranged from good to excellent at effluent discharge points and areas downstream of River Rido, respectively. This might be attributed to the effect of dilution from rainfall. It is therefore recommended that wastewater effluent from the refinery and northern noodles be properly treated before discharged into the study area.

KEYWORDS: Industrial effluent; urbanization; water quality; downstream impact; water quality index

1. Introduction

Economic development and expanding land use activities are directly linked to an increase in waste production. Similar observations were reported by [1-4]. According to Camara et al. [6],
the higher percentages of land use associated with human activities and economic development in watersheds are often interrelated with high concentrations of water pollutants, while undeveloped areas such as natural forest areas are linked with good water quality. As a settlement becomes more urbanized and industrialized, the propensity for waste generation and associated environmental effects, in particular surface water pollution, are expected to be on the rise. One of the major sources of serious pollution problems around the world, particularly in developing countries, is the direct (point pollution) or indirect (non-point pollution) discharge of untreated industrial effluents [5-7]. In Nigeria, this is a huge problem owing to the weak institutional framework and sustainable policies for proper waste management and effective industrial waste treatment facilities and the fact that most industries do not have proper waste treatment plants. In a similar study, [8] found that in many low-income nations, industrial and environmental standards are non-existent, and where they are available, the mitigation instruments are inefficient. Godfrey et al. [9] attributed this to the lack of a reliable and extensive monitoring system for industrial emissions as well as enforcement of compliance with the industrial standards. In another study, [10] reports that most quantities of wastewater generated in developing countries do not undergo any form of treatment. Furthermore, while various types of wastewater treatment facilities (WWTFs) exist in a few urban areas, the majority of them produce untreated effluents that are discharged into freshwater courses [11]. Industrial waste-water originates from the wet nature of industries that usually require large quantities of water for processing and disposal of waste. Hence, most industries are located near water sources. Wastes entering these water bodies are usually in both solid and liquid forms and contain elevated amounts of both inorganic and organic chemicals and their by-products, which are often disposed of in unlined channels and streams. As a result, water bodies, which are major receptacles of treated and untreated or partially treated industrial waste, have become highly polluted [12].

In Nigeria, studies have shown that most of the water bodies are the endpoints of effluents discharged by industries [13–15]. These effluents contain toxic and hazardous materials that settle in river water as bottom sediments and constitute health hazards to the population that depends on the water as a source of supply for domestic uses [16]. Heavy metals are known to be persistent in industrial effluents and can become bioavailable for uptake by other aquatic organisms under favorable conditions. Health challenges like genetic mutation, deformation, cancer, kidney problems, etc., have been linked to pollution by heavy metals [17-19]. The outbreaks of water-borne diseases like cholera, hepatitis, gastro-enteritis, etc., have also been reported as a result of the ingestion of effluent polluted water [20-21].

The study area is River Rido in the Chikun Local Government Area, southern Kaduna. Along the river course are the Northern Noodles Company and the Kaduna Refinery (Nigerian National Petroleum Corporation, NNPC), both of which discharge their effluents into the Rido River. Owing to this prevailing situation, and in view of the fact that Kaduna South has witnessed unprecedented expansions in residential and commercial land use activities [22], there is a need to examine the downstream effects of effluents from these industries on some physicochemical parameters of the Rido River. This will ascertain the nature of the river Rido's response to effluent discharge based on the river’s quality index and increase advocacy on the need for effluent treatment, recycling and regulations by regulatory bodies before discharge into the study area. Findings from this study are also important given settlements around the river's water to meet domestic needs as well as for irrigation. Hence, the aim of the present
study is thus to examine the effects of industrial effluent discharge on some physicochemical parameters and water quality index of the Rido River, Kaduna State, Nigeria.

2. Materials and Methods

2.1. Study Area

River Rido is located in the southern part of the Kaduna metropolis in Chikun Local government area and it is geographically located at Latitude 9°03' N and 11°32' N north of the equator and Longitudes 6°05'E and 8°38'E East of the Greenwich meridian. The area occupies the total area of about 260 km² (Fig 1).

![Figure 1. The Study Area (Kaduna State Showing Chikun LGA).](image)

The climate of the study area is marked by distinct wet and dry seasons. The two seasons are determined by the two prevailing air masses blowing over the area at different periods during the year. The tropical continental air mass brings the dry season while the tropical maritime air mass brings the wet season [23]. The wet season begins in April and ends in October, while the dry season is from November to March. The average annual rainfall ranges between 1000 mm and 1350 mm, respectively. The study area experiences high temperatures all year round, which is a characteristic of the tropics. The mean daily temperature ranged from 27 to 33°C [23]. In terms of economic activities, the predominant land uses in the study area include farming and industrial activities. The industries such as the Northern Noodles, Kaduna refinery and residential settlements generate large quantities of effluents which are mostly discharged into the water bodies, thereby resulting in water contamination. The study area is an agrarian-based economy with agriculture as its major economic activity, which serves as the bedrock of
other activities such as food and cash crop production, livestock rearing, poultry trading, and craft making. Animals such as cattle, sheep, goats, pigs, and poultry are predominantly reared.

1.1. Data collection techniques

A total of eleven (11) points were established at different points along the River Rido. These include the northern noodle discharge point, the Kaduna refinery discharge point, as well as points downstream of the River Rido (points D-K). An interval of 100 m between sampling points was adopted to achieve an even representation of sampling points. A control point was also established 100 m above the industrial area (Fig. 2). The collections were done at a depth of 20–30 cm directly into clean amber bottles at an interval of 100 metres. Sampling was carried out from December to February. pH, free dissolved carbon dioxide, alkalinity, hardness, sodium (Na), electrical conductivity, total dissolved solids, turbidity, total suspended solids, total phosphate (PO$_4^{3-}$), nitrate (NO$_3^{-}$), sulfate (SO$_4^{2-}$), and dissolved oxygen (DO) were the physicochemical parameters studied. On the whole, three (3) samples (Dec-Feb) were collected for each of the eleven (11) sampling points, making a total of thirty-three (33) samples for the entire sampling point.

![Figure 2. Sampling Locations along River Rido.](image)

In-situ analysis of fast changing parameters such as pH, turbidity and electrical conductivity was determined by using handheld in-situ water sampling meters such as the ATI Orion pH meter and conductivity meter at the various sampling points. This in-situ measurement was done because these parameters have extremely low stability [24]. Separate samples were also collected in clean plastic bottles and taken to the laboratory for metal and
microbiological parameter analysis. All plastic bottles (1 l) were first soaked with 50% HNO₃, then rinsed with de-ionized water before being rinsed with water from the control point, because the bottles needed to be clean in the laboratory and then brought to sampling sites. At the sampling site, the bottles were rinsed with water. The bottles were marked for identification using the labels for location and month. The samples were transported to the laboratory in an insulated box to prevent external factors like high temperatures from changing some of the water parameters. Analysis commenced within 12 hours of sampling using the Association of Official Analytical Chemists (AOAC) [25-35] at the National Agency for Food and Drug Administration and Control (NAFDAC), Kaduna Laboratory Services. In Table 1, the analytical techniques used in the study are presented.

| No | Parameter                  | Standard Codes/ Unit | Principles of Measurement            | References |
|----|----------------------------|----------------------|--------------------------------------|------------|
| 1  | Free Dissolved Carbon-dioxide | H₂CO₃                | Titration                            | [36]       |
| 2  | Total Alkalinity           | CaCO₃                | Titration                            | [37]       |
| 3  | Total Sodium               | Na (mg/l)            | Titration                            | [38]       |
| 4  | Dissolved Oxygen           | DO                   | Winkler Method (Titration)           | [39]       |
| 5  | Phosphate                  | PO₄³⁻ (mg/l)         | Colorimetric                         | [40]       |
| 6  | Nitrate                    | NO₃⁻(mg/l)           | Colorimetric                         | [40]       |
| 7  | Total hardness             | CaCO₃/mg/l           | AAS                                  | [41]       |
| 8  | Total Solids               | TS (mg/l)            | Gravimetric method                   | [40]       |
| 9  | Total Dissolved Solids     | TDS (mg/l)           | Gravimetric                          | [42,40]    |
| 10 | Sulphate                   | SO₄²⁻ (mg/l)         | Turbidimetric                        | [40,42,43] |

2.1.1. Water quality Index computation WQI.

The WQI model as adopted by [44] 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 \( i^{th} \) 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 [45], the value of \( q_i \) is calculated using the following equation.

\[
q_i = 100 \left( \frac{V_i - V_{id}}{S_i - V_{id}} \right)
\]  

(2)

Where \( V_i \) is the observed value of the \( i_{th} \) parameter, \( S_i \) is the standard permissible value of the \( i_{th} \) parameter and \( V_{id} \) is the ideal value of the \( i_{th} \) parameter in pure water.

All the ideal values (\( V_{id} \)) are taken as zero for drinking water except pH and dissolved oxygen [46]. 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, \( V_{id} \) is given as 14.6 mg/L.
2.1.2. Calculation of unit weight

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

$$W_n = k/S_n$$  \hspace{1cm} (3)

Where $W_n$ = unit weight for nth parameter, $S_n$ = 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.

$$K = \left[ \frac{1}{\sum_{n=1,2,...,n} S_n} \right]$$  \hspace{1cm} (4)

The parameters used in thus study and their computer weights are presented in Table 2, while Table 3 shows the ranges of WQI, the corresponding status of water quality and their possible uses.

| Parameter                | $S_n$ | Recommending Agency for $S_n$ | Computed K | Computer weight (wi) $k/Sn$ |
|-------------------------|-------|-------------------------------|------------|--------------------------|
| Dissolved oxygen-DO    | 3.0   | WHO                           | 0.9        | 0.3                      |
| pH                     | 6.5-8 | WHO                           | 0.9        | 0.128                    |
| Nitrate                | 50    | WHO                           | 0.9        | 0.018                    |
| Total phosphate        | 5.0   | WHO                           | 0.9        | 0.18                     |
| Sulphate               | 250   | WHO                           | 0.9        | 0.0036                   |
| Turbidity              | 5.0   | WHO                           | 0.9        | 0.18                     |
| Total solids (TSS)     | 5.0   | WHO                           | 0.9        | 0.18                     |
| TDS                    | 1000  | WHO                           | 0.9        | 0.0009                   |
| Na                     | 200   | WHO                           | 0.9        | 0.0045                   |

Table 3: Classification of water quality based on weighted arithmetic WQI method [45,47].

| 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.  |

3. Results and discussion

In Table 4, the mean results of physico-chemical across sampling points are presented. The pH ranged from 6.6 to 7.1, which indicates that the water was slightly acidic with occasional slight alkaline conditions. This is expected as rivers flowing through forests are known to be acidic with pH ranging from 4 to neutrality [38]. Friedl et al. [39] and UNEP GEMS/Water Programme [40] reported that the tolerance of individual species may vary, but pH values between 6.5 and 8.5 are usually indicative of good water quality. More so, the pH values were all within the range of 6.5 to 8.5, as recommended in the World Health Organization guidelines.
Similar trends were also reported in the Senqu-Orange River [42], Silva et al. [43], Ros-Villamizar et al [44], and Machado et al. [45] in streams of the Piracicaba River basin, Brazil. Phiri et al [46] also showed that such slightly lower pH values in effluents from beverage factories as in the current study are due to the nature of the raw materials such as enzymes, lactic acid, benzoic acid, and yeasts that are commonly used in such industries. [47] also noted that even within the acceptable pH range, slightly high pH causes water to have a slippery feel, whereas slightly low pH may cause water to have a bitter or metallic taste.

On the other hand, electrical conductivity, on the other hand, ranged from the lowest value of 79 S/cm at the control point to a very high level of 146.3 S/cm at point K, downstream of the study area. Nevertheless, for all the sampling points, EC was within permissible limits. The high mean conductivities at point K could be due to high levels of mineral ions released in the effluent [48]. These results clearly indicate that points along the river with very high EC values are marginally considerably ionized and may have recorded the highest concentration of ions due to excess dissolved solids. This could be due to the mobilization of conducting ions during the decay processes of organic materials in the stream and thermal mobilization of ions as the water temperature increases [49]. The values were, however, lower than those recorded in some streams of the Nakawa-Ntinda industrial area [49]. Similar trends in conductivity were reported in the Kinawataka stream, its tributaries [49] and the inner Murchison Bay of Lake Victoria [50]. Turbidity was significantly higher at the discharge points and in some sections downstream of the study area than at all the other stations sampled. Turbidity is the measure of particles suspended or dissolved in water that scatter light, making the water appear cloudy or murky. Particulate matter can include sediment—especially clay and silt, fine organic and inorganic matter, soluble colored organic compounds, algae, and other microscopic organisms [51].

High levels of total suspended solids increased water temperatures and decrease dissolved oxygen (DO) levels [52]. In addition, some pathogens like V. cholerae, Giardia lambdia and Cryptosporidia exploit the high water turbidity to hide from the effect of water treatment agents and cause waterborne diseases [53]. Consequently, high water turbidity can promote the development of harmful algal blooms [51,54]. It can increase the cost of water treatment for drinking, food processing, harm fish and other aquatic life by reducing food supplies, degrading spawning beds, and affecting gill function [55]. Muwanga and Barifaijo [56], and Walakira and Okot-Okumu [58] recorded very high values of turbidity in effluents from some food industries they speculated that these could be due to decomposing organic matter in the effluents. Similarly, levels of total suspended solid was generally high at all the sampling points as well as above permissible limits for drinking water. Suspended solids in river water are often due to natural causes such as algae, and inorganic materials such as silt and sediment [57]. However, it has also been reported that pollutants such as dissolved metals and pathogens can attach to suspended particles and enter the water [58]. According to Oberrecht [59], this explains why an increase in turbidity and TSS can often indicate potential pollution, not just a decrease in water quality. When the suspended solids concentration is due to organic materials, particularly sewage effluent and decaying organic matter, the presence of bacteria, protozoa, and viruses is more likely [60].
### Table 4. Mean Distribution of sampled Physico-chemical across Sampling Points.

| Sample | CO₂ (ppm) | Alkalinity | Hardness (mg/l) | Na (mg/l) | pH | EC (µ/cm) | TDS (mg/l) | Turbidity (NTU) | TSS (mg/l) | PO₄³⁻ (mg/l) | NO₃⁻ (mg/l) | SO₂⁻ (mg/l) | DO (mg/l) |
|--------|-----------|------------|----------------|----------|----|-----------|------------|----------------|------------|-------------|-------------|-------------|--------|
| A      | 18±2.0    | 42±0.0     | 34.6±1.2       | 60±0.0   | 7.1±0.05 | 79±19.3   | 114±3.6   | 3.3±1.25       | 23±8.18   | 0.23±0.057   | 12±2.0     | 11.6±2.9    | 8.16±1.2 |
| B      | 16±2.0    | 30±2.0     | 61.3±1.154     | 73.4±12.0| 6.8±0.02 | 85±58.1   | 117±1.0   | 5.46±0.7      | 54.7±7.1  | 0.26±0.31    | 14.3±3.2   | 21.3±2.3    | 4.9±1.2  |
| C      | 16±0.0    | 26±2.0     | 60±0.0         | 53.3±12.0| 6.7±0.02 | 119.7±6.8 | 114.3±4.9 | 10.1±7.2      | 47.3±35   | 1.0±1.1     | 11±1.7     | 33.2±4.0    | 2.86±0.8 |
| D      | 22±2.0    | 32±0.0     | 67.7±1.15      | 60±0.0   | 6.7±0.06 | 139±29.1  | 114±3.6   | 2.5±0.56       | 14±9.5    | 0.12±0.16   | 18±5.0     | 21±3.6      | 1.7±0.7  |
| E      | 18±0.0    | 36±2.0     | 44±2.0         | 140±0.0  | 6.7±0.0  | 137.7±4.2 | 116.3±1.52 | 3.6±1.48       | 35.7±15   | 0.24±0.24   | 14±4.0     | 21.7±0.57   | 2.33±1.2 |
| F      | 18±0.0    | 30±0.0     | 58±2.0         | 113.3±11.5| 6.7±0.012| 148±21.7  | 118.3±5.5 | 4.7±2.3        | 47±23.4   | 0.7±1.03    | 10±3.2     | 23.6±5.5    | 2.1±0.06 |
| G      | 21.3±1.2  | 36±0.0     | 58±0.0         | 226.7±11.6| 7.0±0.01 | 147±30.4  | 144.4±43.4 | 3.2±1.1        | 31±11     | 0.8±0.88    | 13±5.5     | 12.7±1.2    | 2.23±0.98|
| H      | 42±2.0    | 38±2.0     | 56.7±1.155     | 80±0.0   | 6.8±0.01 | 144.7±23.5| 187±8.32  | 16.9±21.8      | 56.3±28   | 0.63±0.25   | 16±2.0     | 10.7±1.2    | 1.9±0.87 |
| I      | 24±0.0    | 40±4.0     | 48±2.0         | 126.6±11.6| 6.6±0.02 | 127±8.2  | 189.6±6.8 | 4.4±1.7        | 41.7±22   | 0.47±0.15   | 16.3±1.15  | 15.8±7.4    | 1.7±0.6  |
| J      | 16±2.0    | 42.7±1.2   | 62±0.0         | 60±0.0   | 6.8±0.0  | 122.3±1.15| 183±28.7  | 2.6±0.49       | 20.6±0.6  | 0.56±0.47   | 14±5.9     | 14±5.2     | 2.4±0.85 |
| K      | 28±0.0    | 46.7±1.6   | 50±0.0         | 280±20.0 | 6.9±0.02 | 146.3±18.8| 173±14.5  | 7.5±2.9        | 46±42     | 0.38±0.38   | 19.3±6.43  | 19.3±6.4   | 2.6±0.95 |

| WHO MPL | NA      | NA      | NA      | 200     | <8      | 400      | 1000     | 5.0      | 5.0      | 5.0      | 50      | 250      | 3.0     |
| NSDWQ MPL | NA   | NA   | NA   | 150   | 6.5-8.5 | 1000 | 500 | 5.0 | 5.0 | 5.0 | 50 | 250 | NA |

A: Control point; B: Northern noodles effluent discharge point; C: Refinery effluent discharge point; D-K Locations Downstream
These organic suspended solids are also more likely to decrease dissolved oxygen levels as they are decomposed [52], although the magnitude of these effects depends on the concentration, duration of exposure, chemical composition, and particle size distribution of the solids, but also varies between organisms and between environments [61]. With the exception of the control point, DO levels were generally low and an indication of pollution. DO is the amount of oxygen in aquatic environments that is accessible to fish, invertebrates, and all organisms in the water [62]. Most aquatic plants and animals require oxygen to survive; fish, for example, cannot survive in water with less than 5 mg/L dissolved oxygen [63]. The low level of dissolved oxygen in water is a sign of contamination and is an important factor in determining water quality, pollution control, and treatment processes [64]. Dissolved oxygen assists in regulating metabolic processes in plant and animal communities and also acts as an indicator of pollution in aquatic ecosystems [65]. The decreased dissolved oxygen could be traceable to the release of hot waste water from the industry [66].

Dissolved oxygen varies depending on temperature. The solubility of oxygen decreases as temperature increases [67]. Also, the effect of oxidation-reduction on residual chemical compounds in the wastewater from the industry could also be responsible for the low concentrations of dissolved oxygen. This agreed with the findings of Aniyikaiye et al. [4]. Phosphate, sulfate, and nitrate levels which were within permissible limits for drinking water have also been linked to waste water [68]. For example, [69] attributed phosphate in water bodies to location, population density, intensive agricultural and industrial activities in its vicinity, rock type of the area, atmospheric deposition, and chemical weathering of bedrock. Similarly, [70] linked phosphate contamination to human and animal waste, industrial chemicals and detergents, and agricultural run-off. The fact that the study area is a receptacle of effluents from the Northern Noodles Company and the Kaduna Refinery (Nigerian National Petroleum Corporation), makes it susceptible to phosphate pollution in the future if the present trend continues unabated. The susceptibility of the study area to phosphate contamination was compounded by the increasing agricultural land-use activity within the study, expanding settlements and a human population that is mostly farmers.

Naturally occurring levels of phosphates in surface and groundwater bodies are not harmful to human health, animals or the environment [69]. Conversely, extremely high levels of phosphates can cause digestive problems [71]. Furthermore, excessive amounts of phosphates in water bodies can lead to eutrophication, a condition of accelerated algal production in extreme quantities until they die off. Also, algal blooms have been linked to health problems such as skin irritation and death (of both humans and animals) depending on the type and duration of exposure [72]. According to Yu et al. [73], sources of nitrates in groundwater and surface water include agrochemicals, surface runoff from irrigated lands, septic tanks, leakage from drainage networks, livestock wastes, manure storage, landfills, urban fertilizer use, industrial wastewater, sludge disposal, etc. Consuming too much nitrate has been linked to methemoglobinemia, including decreased blood pressure, increased heart rate, headaches, stomach cramps, and vomiting [74]. Other symptoms include anemia, cardiovascular disease, sepsis, glucose-6-phosphate-dehydrogenase deficiency, and other metabolic problems [75]. Natural sources of dissolved SO$_4^{2-}$ in freshwater ecosystems include mineral weathering, volcanic activity, decomposition and combustion of organic matter, oxidation of sulphides, and sea spray aerosols [76]. However, acid mine drainage, fertiliser leaching from agricultural soils, wetland drainage, agricultural and industrial wastewater runoff
as well as sea level changes are the main direct and indirect sources of the anthropogenic SO$_4^{2-}$ input to water bodies [77].

Comparison of concentration levels of physico-chemical parameters between points across the study area showed a statistical difference in the concentration levels between control point and effluent discharge point as well as between control and areas downstream of the study area. However, concentration levels were seen to be similar between mean discharge points and areas downstream of the study area, an indication of contamination of downstream by effluent discharge upstream of the study area (Table 5).

|                      | CO$_2$ | Alk | Hardn | Na | pH | EC | TDS | Turb | TSS | PO$_4^{3-}$ | NO$_3^-$ | SO$_4^{2-}$ | DO | P-value 0.05 |
|----------------------|--------|-----|-------|----|----|----|-----|------|-----|--------------|-----------|-------------|----|--------------|
| Mean Effluent Discharge Points | 16.0   | 28  | 60.7  | 63.3 | 6.7 | 102| 116 | 7.8  | 51  | 0.65         | 12.7      | 27.3        | 3.0 | 0.042        |
| Mean Control point    | 18     | 42  | 34.7  | 60  | 7.1 | 79 | 114 | 3.3  | 23  | 0.23         | 12        | 11.7        | 8.2 |              |

Table 5. Students’-test for differences in physico-chemical levels at different sampling points.

|                      | CO$_2$ | Alk | Hardn | Na | pH | EC | TDS | Turb | TSS | PO$_4^{3-}$ | NO$_3^-$ | SO$_4^{2-}$ | DO | P-value 0.05 |
|----------------------|--------|-----|-------|----|----|----|-----|------|-----|--------------|-----------|-------------|----|--------------|
| Mean Effluent Discharge Points | 16.0   | 28  | 60.7  | 63.3 | 6.7 | 102| 116 | 7.8  | 51  | 0/65         | 12.7      | 27.3        | 3.0 | 0.078        |
| Mean Downstream Points (D-K) | 23.7   | 37.7| 55.4  | 136 | 6.8 | 139| 154 | 5.7  | 36.6| 0.49         | 15.4      | 17.4        | 2.11|              |

|                      | CO$_2$ | Alk | Hardn | Na | pH | EC | TDS | Turb | TSS | PO$_4^{3-}$ | NO$_3^-$ | SO$_4^{2-}$ | DO | P-value 0.05 |
|----------------------|--------|-----|-------|----|----|----|-----|------|-----|--------------|-----------|-------------|----|--------------|
| Mean Control point    | 18     | 42  | 34.7  | 60  | 7.1 | 79 | 114 | 3.3  | 23  | 0.23         | 12        | 11.7        | 8.2 | 0.019        |
| Mean Downstream Points (D-K) | 23.7   | 37.7| 55.4  | 136 | 6.8 | 139| 154 | 5.7  | 36.6| 0.49         | 15.4      | 17.4        | 2.11|              |

Difference is statistically significant at 0.05 level of confidence.

To buttress these findings, table 6 compared levels of physico-chemical parameters at discharge points and permissible limits for drinking water by WHO and NSDQW. The result further revealed a significant difference in concentration levels at a 0.05 level of confidence. Because industrial effluent is known to cause changes in the physicochemical parameters of water bodies [46,78,79], the fact that concentration levels downstream of River Rido differed significantly from observations at the control point while remaining similar to observations at the discharge point was expected. The discharge of industrial effluent into rivers, which causes pollution, has also been reported for selected provinces in South Africa [11,79] and rural Poland [80]. In Nigeria, studies have also reported changes in downstream water quality due to the discharge of untreated industrial effluents [81,82]. On the health effects of effluent-polluted water Wang et al. [83] showed that casual disposal of industrial waste can result in waterborne diseases such as diarrhoea, giardiasis, typhoid, cholera, hepatitis, jaundice, and cancer. Furthermore, the effects of untreated wastewater discharge on human health in India [84,85], active pharmaceutical ingredient dilution in freshwater systems in low and low-middle income countries [86,87], and the potential effect of developing municipal wastewater treatment infrastructure in China [88] have all been studied.
Table 6. Students’-test for difference in physico-chemical levels between Mean effluent discharge points and WHO Standards and between Mean downstream points and WHO Standards.

| Parameter | Observed values ($y_i$) | Standard values ($s_i$) | Unit weights ($w_i$) | Quality rating ($q_i$) | $w_i q_i$ | Interpretation |
|-----------|-------------------------|-------------------------|----------------------|-----------------------|----------|----------------|
| DO mg/l   | 3.9                     | 3.0                     | 0.3                  | 90                    | 27       | Good           |
| pH        | 6.7                     | 7.5                     | 0.128                | 60                    | 7.7      | Excellent      |
| Nitrate mg/l | 12.7                  | 50                      | 0.018                | 25.4                  | 0.46     | Excellent      |
| Phosphate(PO₄³⁻) mg/l | 0.65                 | 5.0                     | 0.18                 | 13                    | 2.34     | Excellent      |
| Sulphate mg/l | 27.3                   | 250                     | 0.0036               | 10.9                  | 0.04     | Excellent      |
| Turbidity NTU | 7.8                   | 5.0                     | 0.18                 | 156                   | 28.08    | Good           |
| TSS mg/l  | 51.0                    | 5.0                     | 0.18                 | 1020                  | 183.6    | Poor           |
| TDS mg/l  | 115.7                   | 1000                    | 0.009                | 11.59                 | 0.01     | Excellent      |
| Na mg/l   | 63.3                    | 200                     | 0.0045               | 31.8                  | 0.14     | Excellent      |

$\sum_{i=1}^{n} w_i - q_i = 27.7$

Table 7. Water Quality Index (WQI) of physico-chemical parameters at effluent discharge points in River Rido.

In Tables 7 and 8, the results of water quality index of physico-chemical parameters at both effluent discharge points and areas downstream of River Rido shows that the quality of the river ranged good to excellent at effluent discharge points and areas downstream of River Rido respectively. This findings when compared to the observed levels of specific quality parameter of the study area might differ. According to Uddin et al., [88], one of the problems of the WQI model is that it is usually developed based on site-specific guidelines for a particular region, and are therefore not generic. Moreover, they produce uncertainty in the conversion of large amounts of water quality data into a single index. Similarly [89] also showed that, water quality index (WQI) has often been misconstrued to mean water quality standards (WQSs). Although both are concepts used in water quality monitoring and assessment, they are fundamentally different. Water quality index has therefore been seen as priceless and matchless evaluation set up to depict the overall water quality status in a single term that is helpful for the selection of right management modus operandi to meet the concerned issues [89].

The objective of the WQI is to classify the waters relative to biological, chemical and physical characteristics defining their possible uses and managing their allocations [90,91]. A
number of water quality parameters are included in a mathematical equation to rate water quality, determining the suitability of water for drinking [91,92]. Conversely, water quality standards are governance frameworks covering specific uses and water quality criteria to save uses from gratuitous harm (United States Environmental Protection Agency - USEPA, [93]). The decisive factor espoused and integrated into the standards are the tolerable concentration of pollutants in states, territories and certified clannish waters [94]. Thus, while water quality index portrays the combined influence of diverse water quality indicators and conveys water quality issues to the public and legislative decision makers [89], water quality standards depicts the scientifically established targets approved by regulatory agencies for different water uses (World Health Organization) [94].

Table 8. Water Quality Index (WQI) of physico-chemical parameters at downstream points in River Rido (D-K).

| Parameter       | Observed values ($v_i$) | Standard values ($s_i$) | Unit weights ($w_i$) | Quality rating ($q_i$) | $w_iq_i$ | Interpretation |
|-----------------|-------------------------|-------------------------|---------------------|------------------------|----------|----------------|
| DO mg/l         | 2.1                     | 3.0                     | 0.3                 | 108                    | 32.4     | Good           |
| pH              | 6.8                     | 7.5                     | 0.128               | 40                     | 5.12     | Excellent      |
| Nitrate mg/l    | 15.4                    | 50                      | 0.018               | 30.8                   | 0.55     | Excellent      |
| Phosphate(PO$_{4}$) mg/l | 0.48 | 5.0                  | 0.18                | 9.6                    | 1.73     | Excellent      |
| Sulphate mg/l   | 17.4                    | 250                     | 0.0036              | 6.96                   | 0.025    | Excellent      |
| Turbidity NTU   | 5.7                     | 5.0                     | 0.18                | 114                    | 20.5     | Excellent      |
| TSS mg/l        | 36.5                    | 5.0                     | 0.18                | 730                    | 131.4    | Poor           |
| TDS mg/l        | 156.3                   | 1000                    | 0.009               | 15.4                   | 0.014    | Excellent      |
| Na mg/l         | 135.8                   | 200                     | 0.0045              | 67.9                   | 0.305    | Excellent      |

$\sum_{i=1}^{n} w_i - q_i = 21.3$

4. Conclusions

Unregulated urbanization and population expansion is among the issues that slowing the attainment of key sustainable development Goals in most development Countries. Water pollution, changing climatic patterns, waste management problems etc, are some of the indictors of an expanding urban settlement, and this reflect the situation in the study area. More so, moste developing countries such as Nigeria still lack the capacity to regulate some land use activities are that are unsustainable as well as have the potential to degrade the natural environment. The study area is economically developed and densely populated and hence plays an important role in the economic development of the entire State. This mostly due to the availability of the water body (Rido River) which promotes agricultural activities as well as serve as source of water supply for industrial and domestic uses. One of such evidence is the location of industries in the upper reaches of the study area, whose effluents are discharged into River Rido, hence resulting changes in the physicochemical quality of the river water, downstream of the study area. For example mean levels of turbidity total suspended solids, total phosphate and dissolve oxygen at effluent discharge points, as well as in most areas downstream of the study area were generally above permissible limits for drinking water. The comparison of the levels of physico-chemical parameters at discharge points with permissible limits for drinking water by WHO and NSDQW, showed significant differences in concentration levels at 0.05 level of confidence. In addition, statistical differences were observed in the concentration levels of investigated parameters, between control point and effluent discharge points, as well as between control point and areas downstream of the study.
area. However, concentration levels was seen to be similar between discharge points and areas downstream of the study area, an indication of contamination at the downstream by effluent discharge upstream. It is therefore recommended that wastewater effluent from refinery and northern noodles be properly treated before discharge into River Rido and/or any other water bodies in the study area. More so, environmental safety awareness and sensitization programmes should be organized more so as to educate the people on the importance of reducing water pollution.

**Author Contributions**

Ali Williams Butu is the Principal Investigator and was part of the project conception up to analysis. Chukwudi Nnaemeka Emeribe and Ijeoma Obianuju Muoka were project coordinators and part of the project conception and report writing. Oluchi Favour Emeribe, and Emmanuel Temiotan Ogbomida handled statistical analysis and interpretations and were part of the conception of the project and report writing.

**Acknowledgments**

The authors wish to acknowledge the Technical Assistance of the Laboratory Unit of National Agency for Food and Drug Administration and Control (NAFDAC), Nigeria, during the analysis of samples.

**Conflict of Interest**

The authors declare there is no conflict of Interest.

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