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Statistical evaluation of surface water quality parameters: the extent of industrial effluent pollution in urban settlement

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ARTICLE INFO	ABSTRACT
	BACKGROUND AND OBJECTIVES: Industrial effluent contamination of water resources has emerged as a major challenge in developing and densely populated countries like Nigeria where river systems are the primary means for disposal of waste, especially the effluents from surrounding industries. This study seeks to determine the extent of surface water pollution from industrial effluent discharge. **METHODS:** Principal Component Analysis (PCA) and analysis of variance (ANOVA) were applied on the surface water quality data to identify the pollution sources and their contribution toward water quality variation. Water samples were collected from 4 sampling locations along the Onne-Okirika river. **FINDINGS:** The characteristics of the river showed a mean concentration of biochemical Oxygen Demand (BOD = 19.73 mg/l), Chemical Oxygen Demand (COD = 54.53 mg/l), Ammonia (NH3 = 21.00 mg/l), Dissolved Oxygen (DO = 5.78 mg/l) and temperature (28.40ºC) which varied significantly among sampling locations. Site 1, 2, and 3 showed a high level of NH3 and Chemical Oxygen Demand while site 4 (the control) has slightly high salinity when compared. The extent of pollution could be classified as; site 1 (High Pollution), site 2 (Moderate Pollution), and site 3 (Low Pollution). **CONCLUSION:** Sources of pollution include effluents from industrial plants such as fertilizer plants and oil refineries due to the high level of NH3. While the higher Chemical Oxygen Demand level is an indication of a greater amount of biodegradable organic material, which reduced the amount of Dissolved Oxygen. Additionally, a reduction in Dissolved Oxygen level can lead to an anaerobic condition, which is insidious to aquatic life forms. Therefore, the state environmental regulatory agency should ensure compliance monitoring of the industry's activities.

NUMBER OF REFERENCES	NUMBER OF FIGURES	NUMBER OF TABLES
30	4	6

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INTRODUCTION

Rivers play a significant role as they serve not only the purpose of water supply for domestic, industrial, agricultural and power generation but also utilized for the disposal of industrial waste and therefore put under tremendous pressure (Subin *et al.,* 2013). The pressure of increasing population, growth of industries, inadequate environmental awareness, lack of enforcement of environmental regulations, untreated effluent discharge from industries and municipalities, use of chemical fertilizers, etc. are the major causes of water pollution (Monte-Egito *et al.,* 2007). The pollution of water resources is a global issue (Vargas *et al.,* 2001; Ohe *et al.,* 2003; Monte-Egito *et al.,* 2007; Sandra *et al.,* 2010). In addition to the direct health effects, pollutants may be mutagenic or toxic and could lead to human afflictions such as cancer, atherosclerosis, cardiovascular diseases, and premature aging. It is required that surface water parameters must meet acceptable limits and minimum ecological criteria (McKnight *et al.,* 2010). The pollutants from industrial discharge besides finding their way to surface waters and rivers may also percolate into sub-surface to contaminate groundwater sources. The quality of surface water provides significant information about the available resources for supporting life in the ecosystem (Leme and Marin-Morales, 2009; Manikannan *et al.,* 2011). The physical, chemical, and biological composition of surface water is controlled by many factors such as natural (climate, topography, and precipitation) and anthropogenic (domestic, industrial activities, and agricultural run-off). Increasing surface water pollution causes not only the deterioration of the water quality but also poses a great threat to human health, aquatic life, economic development, and social prosperity (Ohe *et al.,* 2003; Milovanovic, 2007). It is, therefore, imperative to prevent and control surface water contamination and to make a proper investigation of its quality for effective management (Singh *et al.,* 2005). Several researchers have used Principal Component Analysis (PCA) and Analysis of Variance (ANOVA) to identify water quality sources and compare their characteristics. Shrestha and kazama (Stambuk-Giljanovic , 1999; Shrestha and Kazama, 2007), Huang *et al.* (2010) and Juahir *et al.* (2011) studied spatial variability of surface water quality and sources apportionment and classified the studied water bodies into high pollution site (HP),

Moderate pollution site (MP) and Low pollution site (LP). Onojake *et al.,* (2011) reported that rivers in the Delta State of Nigeria were heavily polluted as a result of industrial discharge which is an anthropogenic source of pollution. They used Principal Components Analysis (PCA) to identify the latent factors that explain the chemistry of the surface water in which PCA yielded three Principal Components with more than 82% variance. However, this study seeks to determine the extent of surface water pollution from industrial effluent discharge into the Onne-Okirika river within urban settlement. The current study has been carried out in Port Harcourt in 2020.

MATERIALS AND METHODS

Description of the study area

The Onne-Okrika River flows from the Okrika creek into the main sea at the Onne seaport. The main source of the river is the Bonny River. There is mangrove vegetation around the banks of the river. People who live in communities around the river are mostly fishermen and farmers. Local fishing ports can be sighted along the bank of the river. Water from the river is also used for irrigation by farmers who farm along the bank of this river. So, economically the river serves as a means of livelihood for people who fish and those who depend on the river for growing their crops, especially in the dry seasons. The Onne-Okrika River is confined in the saltwater swamp zone and is influenced by tidal fluxes. The flow of the Onne-Okrika creek is only slightly swift and the bidirectional two major industries that discharge their effluent into this River are the Port Harcourt Refinery and the surrounding fertilizer industry. This study seeks to investigate the impact of industrial effluent discharge at the Onne-Okrika River.

The surrounding Industry is located in Onne (8° 350' N and 7°925' N, 5° 162' E and 5° 215' E) in urban area, present Eleme Local Government Area of Rivers State. They produce Urea fertilizer, ammonia, demineralized water, and generate power. The sampling points are numbered 1, 2, 3, and 4 on the map in Fig. 1.

Sample Collection and Analysis

Four sites were established along the Onne-Okrika river for water sampling. Site 4 is about 280m away from the industry's effluent discharge point upstream, used as the control. Site 1 is at the
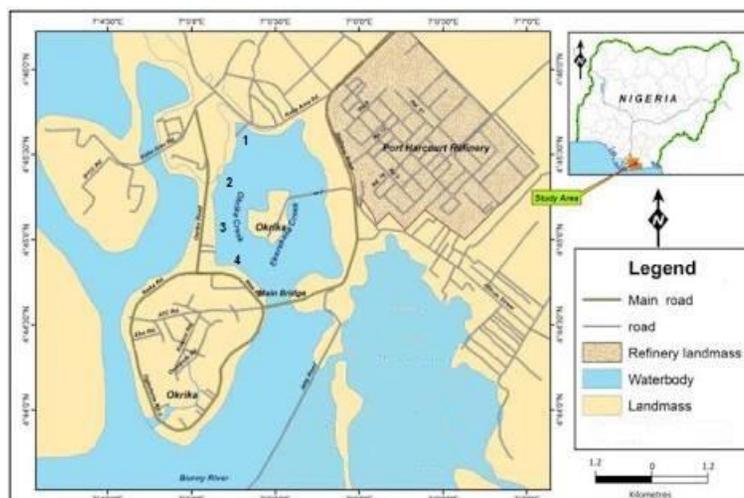
Fig. 1: Map of study area showing the sample collection points

Table 1: Sample location

Location	Distance between Sample collection points
Site 1	Industry's effluent Discharge Point
Site 2	120 meters away from site 1 downstream
Site 3	150 meters away from site 2 downstream
Site 4	280 meters away from industry's discharge point upstream

industry's discharge point. Site 2 is located at 120m from Site 1 and site 3 is 150m from site 2 (Table 1). The control site was selected as the least polluted site owing to the absence of effluent discharge in the direct vicinity. The sampling was carried out over three months. Samples were collected from each site once in a month. The control Sample at site 4 is the water in its natural state (i.e. before the effluent discharge on the water surface) (Table 1). The sample was sent to the laboratory immediately after collection. The temperature of the sample was measured with a mercury-in-glass thermometer; the bulb of the thermometer was completely immersed in water to a depth of 15 cm and remained for about 3-5 minutes. The temperature of the water was taken when the mercury level became steady. Winkler titrimetric method was used to analyze water samples for Dissolved Oxygen (DO). Biochemical Oxygen Demand (BOD) was determined by the dilution winkler method. Chemical Oxygen Demand (COD) was determined (alpha, 1998) method. Ammonia was

measured by nessler's colorimetric method. Salinity as chloride content of the samples was determined according to APHA-4500B while Total Dissolved Solids (TDS) was determined according to APHA 20gc using TDs meter after due calibration. Measurement of Total Hardness was done by EDTA titrimetry. The pH of the sample was measured by the electrometric method. Details of the method used to determine the concentration of BOD, Ammonia, Total hardness, and pH are contained in Etim and Onianwa (2013) report.

Principal Component Analysis (PCA)

Principal Component Analysis (PCA) is one of the best multivariate statistical techniques for extracting linear relationships among a set of variables (Simeonov *et al.,* 2003; Monte-Egito *et al.,* 2007; Yap *et al.,* 2011; Botelho, 2012). It provides data on the significant parameters with minimum loss of original data (Singh *et al.,* 2005). PCA is a recognition tool that attempts to describe the variance of a large data set of inter-correlated variables with a smaller

Table 2: Descriptive statistics of the physicochemical parameters

Parameter	Site 1	Site 2	Site 3	Mean $\pm$ SD	Site 4
Temperature ($^{\circ}$C)	28.95	28.85	27.5	28.43 $\pm$ 0.81	28.10
pH	8.67	8.28	7.75	8.23 $\pm$ 0.46	7.45
DO (mg/l)	9.52	4.26	3.55	5.78 $\pm$ 3.26	5.40
BOD (mg/l)	24.50	18.10	16.60	19.73 $\pm$ 4.20	12.40
COD (mg/l)	60.00	57.10	46.50	54.53 $\pm$ 7.11	37.50
NH_3 (mg/l)	25.10	19.50	18.40	21.00 $\pm$ 3.59	0.00
Salinity (mg/l)	18.90	18.30	18.20	18.47 $\pm$ 0.38	24.70

Table 3: Henry's Law Coefficients, KH (mol/L. atm) (Masters, 2006)

Temperature ($^{\circ}$C)	Oxygen (O_2)
0	0.0021812
5	0.0019126
10	0.0016963
15	0.0015236
20	0.0013840
25	0.0012630

set of variables. In this study, PCA was applied to the surface water quality data from the Onne-Okirika river to identify the source and extent of pollution. The measure of sampling adequacy was obtained by the Kaiser-Meyer-Olkin (KMO) method which is 0.714, indicating that the degree of intercorrelation among the variables and the essence of PCA application was valid. Similarly, the Bartlett test of sphericity was significant (p < 0.0001), confirming that the variables are correlated. The surface water samples were collected from four different sampling points along the Onne-Okirika River. Selected parameters such as Temperature, pH, BOD, DO, COD, NH_3 and Salinity were analyzed to determine the extent of industrial effluent pollution in the river at the different sites, and these parameters were selected based on the composition of the industry's product.

RESULTS AND DISCUSSION
Statistical Analysis

It was observed that DO, BOD, COD, NH_3 concentration and conductivity varied significantly among sampling locations. The descriptive statistics showing the mean and standard deviation of results obtained is presented in Table 2.

All parameters analyzed varied significantly among sampling locations. Excel and SPSS software were used to perform ANOVA between the samples mean and control; it showed a sig. of 0.819, df (1) between groups, and 16 within groups at a 95% confidence level. The method of analysis used in this work is in agreement with Paul and James (2011) who used Excel and Gen stat to perform ANOVA to investigate the impact of industrial effluents on water quality of streams. In their method, differences in concentration levels obtained for a given parameter along sampling locations were considered significant if calculated P-values were < 0.05. Ewa *et al.* (2011), Sum and Gui (2015), Olatunji and Horsfall (2017) also used ANOVA to analyze their water quality parameters. However, most studies did not show the solubility of gases in polluted rivers. Therefore, the linear regression model developed to predict the solubility of gases in rivers and the oxygen deficit calculated herein is the novelty in this study.

Solubility of Gases in the River

The solubility of gases in the river was measured using Henry's Law Coefficient (see Table 3 below).
The solubility of the gas in water is given by Eq. 1

Table 4: Oxygen deficit at different points in the river

Location	Temp (°C)	K_H (mol/L)	DO_s (mg/L)	DO deficit
Site 1	28.95	0.000942	6.33	-3.19
Site 2	28.85	0.000946	6.36	2.10
Site 3	27.50	0.001000	6.72	3.17
Site 4	28.10	0.000976	6.56	1.16
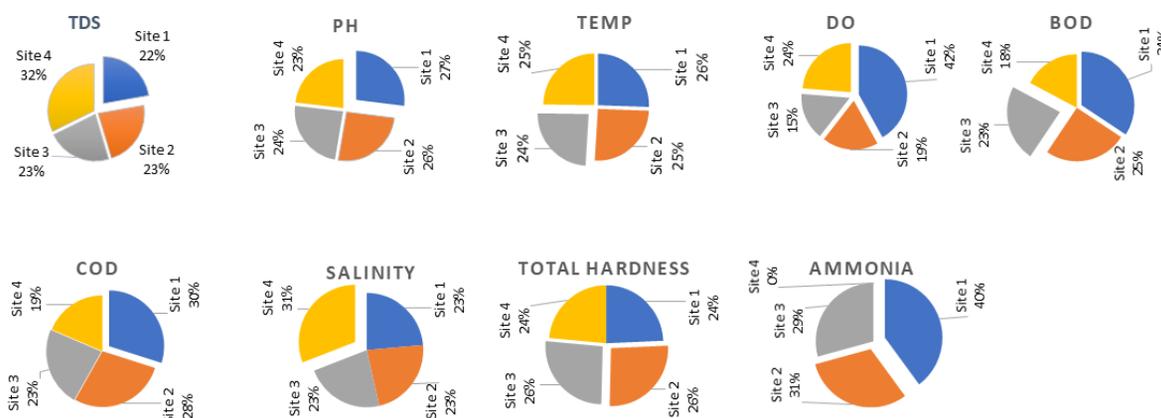
Fig. 2: Variations in physicochemical characteristics of parameters

(Masters, 2006):

$$[\text{gas}] = K_H P_g \tag{1}$$

The linear equation from the Fig. 4C can be used to predict the concentration of oxygen at any given temperature. The graph in Fig. 4C was plotted from Table 3: Henry's law coefficient (Masters, 2006). From Table 3 and Fig. 4C we obtain the regression equation given below (Eq. 2);

$$\therefore K_H = -4 \times 10^{-5} T + 0.0021 \tag{2}$$

The concentration of oxygen in the air is 21% by volume. Therefore, the equilibrium concentration of oxygen in the river in (mg/L) at site 1 with a temperature of 28.95 °C and 1 atm of pressure.

$$K_H = -4 \times 10^{-5}(28.95) + 0.0021 \tag{3}$$

$$K_H = 0.000942 \text{ mol} / L \tag{4}$$

Since air is 21% Oxygen, so its partial pressure at 1 atmosphere is given as:

$$P_g = 0.21 \times 1 \text{ atm} = 0.21 \text{ atm} \tag{5}$$

$$[O_2] = K_H P_g = 0.000942 \frac{\text{mol}}{L}.\text{atm} \times 0.21 \tag{6}$$

$$DO_s = 1.9782 \times 10^{-4} \frac{\text{mol}}{L} \times \frac{32g}{\text{mol}} \times \frac{10^3 \text{mg}}{g} = 6.33 \text{mg} / L \tag{7}$$

The ultimate BOD by Masters (2006) is given as:

$$L = \frac{BOD_5}{\left(1 - e^{-k(t)}\right)} \tag{8}$$

Principal Component Analysis

Principal Component Analysis showing the extent of industrial effluent pollution on the surface water quality: axes F1 and F2 were selected as the observational axes because it carries 99.57% of the initial information (Fig. 3). Therefore, the interpretation will be focused on axes F1 and F2. There is a strong and positive correlation between the water quality at sites 2 and 3 (Fig. 3). However, site 4 shows a significant difference as the control. This indicates

Table 5: Pearson Correlation matrix

Variables	Site 1	Site 2	Site 3	Site 4
Site 1	1.000	0.988	0.975	0.738
Site 2	0.988	1.000	0.994	0.810
Site 3	0.975	0.994	1.000	0.825
Site 4	0.738	0.810	0.825	1.000

Table 6: Eigenvalues

Factors	F1	F2	F3	F4
Eigenvalue	3.6740	0.3090	0.0140	0.0030
Variability (%)	91.845	7.7250	0.3610	0.0690
Cumulative (%)	91.845	99.570	99.931	100.00
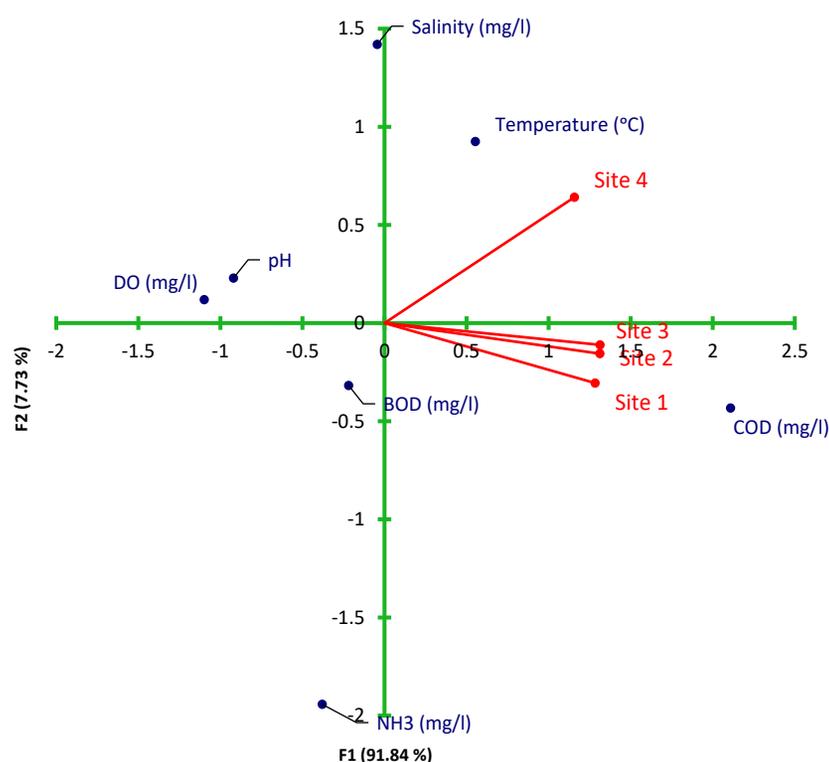
Fig. 3: A biplot of water quality parameters versus sites for axes F1 and F2 at 99.57%

that site 1 has the highest level of contamination, followed by site 2, and then site 3 is slightly polluted because the correlation matrix shows that site 3 has a stronger relationship with site 4 compared to sites 1 and 2 (Table 5). Site 1, 2 and 3, has a high level of NH_3 and COD while at site 4, the salinity is slightly high (Fig. 2). The study revealed a high level of NH_3 and COD. Point sources of NH_3 include effluents from industrial plants such as fertilizer plants and oil refineries (CCME 1989). While High level of COD is an indication of a greater amount of biodegradable organic material in the sample, which can reduce the

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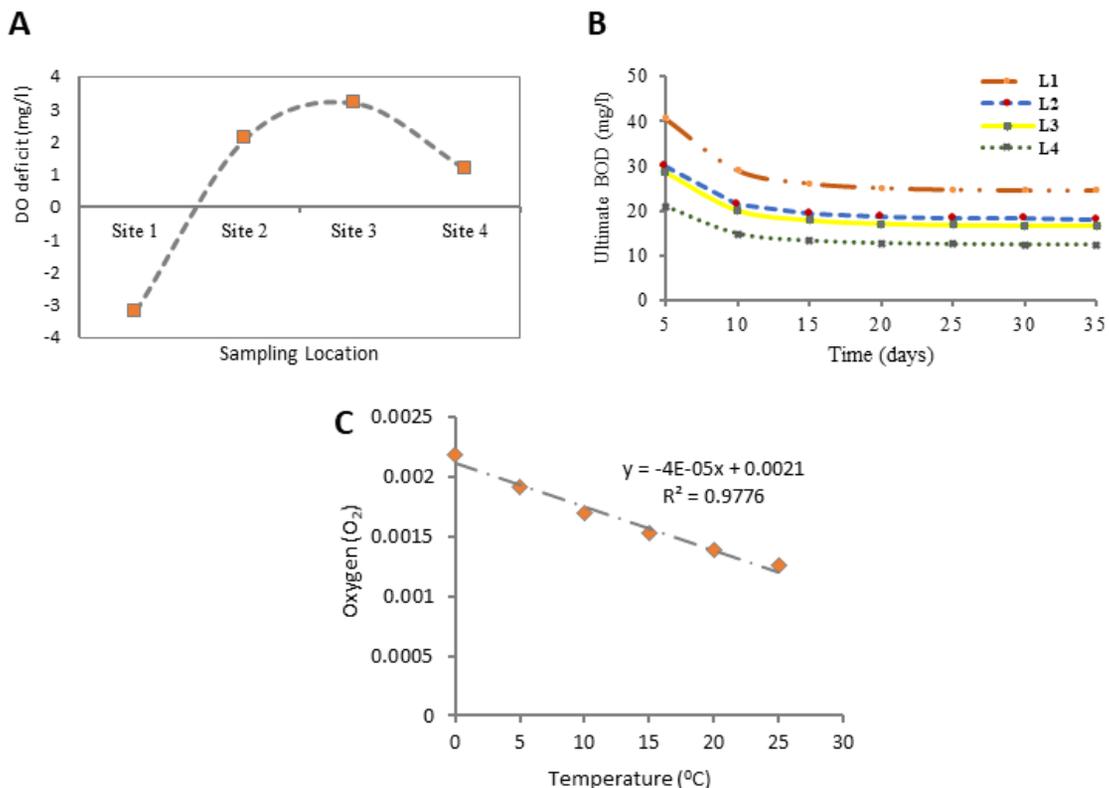
Fig. 4: (A) Variations in dissolved oxygen deficit (B) Variations in ultimate BOD (C) Oxygen coefficient of the river

(DO) levels. A reduction in DO can lead to anaerobic condition, which is detrimental to aquatic life forms (Real Tech 2017).

Industrial effluents are the main sources of direct and often continuous input of pollutants into aquatic ecosystems with long term implications on ecosystem functioning (Masters, 2006). This study revealed a high level of NH_3, BOD, COD, and slightly high pH. The high level of BOD is an indication of the presence of oxygen-demanding waste. However, there is no significant variation in TDS among the sampling locations (Fig. 2a). Again, the pH varied significantly among the sampling locations and the pH of sites 1, 2, and 3 are higher than the control (site 4), this is an indication of pollution (Fig. 2b). Additionally, the concentration of pH declined progressively from 8.7 to 7.8 with distance from the point of impact but were still significantly higher than the control. The variation in pH this affected other chemical reactions such as solubility and metal toxicity (Sayyed and Bhosel, 2010; Sirohi *et al.,* 2014). Metcalf and Eddy

(2003) wrote that the concentration range suitable for the existence of most biological life is quite critical (between 6 and 9). The temperature at sampling locations 1 and 2 are higher site 3 and the control sample which is site 4 (Fig. 2c). The temperature of the water is a very important parameter because of its effect on chemical reactions and reaction rates, aquatic life, and the suitability of the water for beneficial use. Also, oxygen is less soluble in warm water than in cold water. From Fig. 2d, there is a significant variation in DO (dissolved oxygen) among sampling locations. However, the actual quantity of oxygen that can be present is solution is controlled by (1) the partial pressure of the gas in the atmosphere (2) the temperature (3) solubility of the gases, and (4) other impurities in the water such as salinity, suspended solids, etc. The biochemical oxygen demand (BOD) varied significantly among the sampling locations (Fig. 2e). From Fig. 2f, the chemical oxygen demand (COD) varied significantly among the sampling locations. There is no significant

variation in the salinity level of the river among the various sampling locations, the salinity of all three sampling sites (1, 2, and 3) is less than the control (site 4) in Fig. 2g. From Fig. 2h, the total hardness varied significantly among sampling locations. There is a significant variation in ammonia concentration among the sampling locations in Fig. 2i. The average level of a contaminant in the effluent receiving water body within 100 meters around the point of effluent discharge, henceforth referred to as the point of impact (POI), is shown in Fig 2. Higher concentrations of BOD (19.73 mg/l), NH_3 (21.00 mg/l), COD (54.53 mg/l), Total Hardness (4801.13 mg/l), TDS (17042.30 mg/l), Salinity (18.47 mg/l) and high temperature (28.40 °C), DO (5.78 mg/l) and pH (8.20) were observed in the water sample at various locations of the river. The order of abundance is COD > BOD_5 > DO, showing less anthropogenic pressure on the surface water. However, as DO drops, fish and other aquatic life are threatened, it also reduces the attractiveness of the river for recreational purposes.

Oxygen deficit at different points in the river

The oxygen deficit at site 2 and the control site is low compared to site 1 and site 3 (Fig. 4A and Table 4). From Fig. 4B; L1, L2, L3, and L4 represents the Ultimate BOD concentration for site 1, 2, 3, and site 4 respectively. It shows that the ultimate BOD at the industry's discharge point is higher. However, site 2 and site 3 did not show any significant difference. The ultimate BOD values were calculated in Excel, following iterations with time in (days) for all the locations (Fig. 4B).

CONCLUSION

This study has sufficiently analyzed and evaluated the current status of the Onne-Okirika River. The non-variability and low level of TDS among sampled locations is an indication of excessive harmful metallic mineral contaminants from wastewater discharges. It was observed that the average temperature of the river is high. Many varieties of fish and aquatic life are extremely sensitive to changes in water temperature and composition. The observed higher temperatures at sites 1 and 2, maybe attributed to high biological or chemical activities which indicate greater pollutant load at these sections of the river. A BOD value above 8.0mg/l at site 4, shows that the river was severely polluted at the point of impact (POI). Additionally, higher concentrations of NH_3 (21.00 mg/l), COD (54.53 mg/l), Total Hardness (4801.13 mg/l), Salinity (18.47 mg/l), DO (5.78 mg/l) and pH (8.20) were observed at various sampling points of the river. The order of abundance is COD > BOD_5 > DO, showing less anthropogenic pressure on the surface water. However, as DO decreases, fish and other marine life are threatened, it also reduces the attractiveness of the river for recreational purposes. This suggests that communities within the surrounding location should not depend on the river's self-cleansing mechanism for consumption. Therefore, there is need for industries to introduce as well as implement alternative systems to safely discharge their effluents following the environmental regulations. Also, in the case of adopting water bodies like a sink for waste disposal, such industrial effluent should be treated.

CONFLICT OF INTEREST

The authors declare no potential conflict of interest regarding the publication of this work. In addition, the ethical issues including plagiarism, informed consent, misconduct, data fabrication and, or falsification, double publication and, or submission, and redundancy have been completely witnessed by the authors.

ABBREVIATIONS

Symbols

DO_s saturation value of dissolved oxygen

[gas]	concentration of dissolved gas (mol/L)
BOD	biochemical oxygen demand (mg/L)
DO	dissolved oxygen (mg/L)
K_H	henry's law constant (mol/L.atm)
P_g	partial pressure of the gas in air (atm)
POI	Point of impact
O_2	oxygen
N	nitrogen
L	ultimate BOD (mg/L)
COD	chemical oxygen demand (mg/L)
T	Temperature ($^\circ C$)
PCA	principal components analysis
HP	high pollution
MP	moderate pollution
LP	low pollution

Superscripts

k	rate constant (days^{-1})
t	time (days)

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