The Pharmaceutical and Chemical Journal, **2018, 5(3):135-142**

Available online www.tpcj.org

Research Article

ISSN: 2349-7092
CODEN(USA): PCJHBA

An Evaluation of the Level of Some Physicochemical Parameters in the New Calabar River, Rivers State, Nigeria

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Abstract The new calabar river (NCR) is very important to the people of Niger delta because of the pivotal role it plays in the economic development of the place with numerous companies within the vicinity of the river. The quality of water of the river felt threaten with this development. Therefore, some physicochemical parameters of the river were investigated to determine the pollution status of the river with particular reference to physicochemical parameters. Water samples were collected from the river and subjected to standard method of analysis as provided by APHA. The results of the analysis showed the following mean concentrations of the physicochemical parameters: pH (7.46), conductivity (3847.41µS/cm), TDS (417mg/l), turbidity (4.79NTU), salinity (2560.73mg/l), DO (5.8), SO_4^{2-} (22.48mg/l), NO_3^- (20.39mg/l), PO_4^{2-} (0.83mg/l), Cl^- (1557.66mg/l) and total harness (40.29mg/l). Of the twelve physicochemical parameters investigated, only pH, PO_4^{2-}, and total hardness were within the limits set by WHO. The investigation revealed that the NCR is polluted with regard to the physicochemical parameters. It is our view that the operating companies within the vicinity of the river to ensure that their wastes are properly treated before discharged and government should see as a matter of necessity that proper environmental audit is carried out on the river.

Keywords parameter, physicochemical, river, calabar, environment, audit, analysis, pollution, company, location, map, government

Introduction

Waste is produced from every process associated with production and consumption. The pollution of the environment with wastes is a consequence of man's fortitude to match his desire with production through the establishment of industries with high potential to pollute the environment [1]. Nwineewii [2] carried out a study on the assessment of the level of some physicochemical parameters from eleme creeks in Port Harcourt to estimate the impact of the eleme petrochemicals company on the environment. The following mean concentrations of the analysed physicochemical parameters were observed: conductivity (357µS/cm), TDS (181mg/l), temperature (27.3), turbidity (14.43NTU), NO_3^-(0.354mg/l), NH_3(0.163mg/l), TSS (16.99mg/l), pH (7.3) and alkalinity (116.42). It was observed from the study that the concentrations of the investigated physicochemical parameters were high compared with eleme petrochemicals impact assessment study of 1992 but within the limits recommended by WHO. The elevated concentrations of the parameters were attributed to the operational activities of the eleme petrochemicals company and the continuous dredging of the eleme creek. Dienye & Woke [3] studied the physicochemical parameters of New Calabar Rivers across five stations in relation to season from December 2013 to May 2014. Results from this investigation showed that this water was slightly acidic across months with pH range of 6.18 to 7.08 and across stations. Relatively high level of dissolved oxygen (DO) was observed during the study with higher value at the upstream sampled station than downstream sampled stations. The study also revealed that there was no significant variation in temperature and Biochemical Oxygen Demand across stations and seasons. Analysis of surface water pollution from abattoirs and the interrelationship between physicochemical properties of the New Calabar River was carried out by Tekenah et al. [4]. In their research, the effects of discharged untreated abattoir waste on water quality and the interrelationship between analysed physicochemical properties were studied. Correlations were observed between the oxygen availability (BOD/COD) and Cl, Mg as well as Ca ions concentrations. An increase in the salt content of the river was observed to correlate with an increase in total solids (TS) and Total suspended solids (TSS) while the dissolved oxygen content also showed an increasing effect with increasing river pH. The river was assessed to be polluted using Prati et al., [5] classification of surface water quality. The pollution was as a result of discharge of human and domestic wastes into the water body as well as the introduction of the abattoir effluent which had a significant negative effect contributing to the poor health of the river. The industries engaged in the processing of meat in Nigeria are considered as major contributors in the continuous pollution of the water bodies. The water quality of New Calabar river was assessed by Stanley *et al* [6]. The results obtained were compared with the World Health Organization for portable water and conclusions were made that the standards of certain parameters were more than the permissible limits.

Leton and Nwekwe [7] employed the pollution load index techniques to evaluate the water quality status of the New Calabar River. Water quality status was analysed with reference to World Health Organisation standards for domestic water supply and the American Society of Civil Engineers (ASCE) permissible quality of raw water for portable use, given normal treatment. The data obtained were then used for the pollution index (P I) computations. A Pollution index above one (PI > I) indicates that the water source is unacceptable for the particular use.

The river water quality parameters comply to a large extent with most of the set standards. However, it was notably very poor in terms of Biochemical Oxygen Demand (BOD) implying that New Calabar River at the points investigated could be bacteriologically unsafe for human consumption as high BOD indicates high biological activities and possibly pathogenic pollutant. The study also share that pollution index (P1) along the River at Aluu, Choba, Rumuokparli to Egbelu were 1.0124, 1.6098, 1.5030 respectively in terms of numerical values and 1.1209, 1.6160, 1.5611, 11.5543 respectively in terms of relative damage due to pollution. The results indicated that the pollution of Choba was 59 percent than the upstream at Aluu, possibly due to waste inputs from the oil servicing and plastic manufacturing companies.

Study Area

The study area is the New Calabar River (NCR) which is situated between longitude 7°6O'E and latitude 5°45'N in the coastal area of the Niger Delta region of Nigeria and empties into Atlantic Ocean. The river is subject to effluent discharged from industries located along its banks. Surface run-off from soil erosions, lumbering activities, forestry operations, dredging activities may lead to wide scale contamination of the river [3]. NCR receives fresh water, industrial effluent and domestic water from water front settlement and communities along the river [8]. Industries and companies that indulged in the discharge of wastes into the NCR include among others Indomie, Eagle cement, Agip oil, Wilbros Nigeria etc.

Study Approach

The human activities and industrial operations that occur at the various stations of this study accounts for the reason of this investigation. People dwelling along the river are mostly farmers and fishermen whose activities contribute to a large extent in polluting the river. Industrial effluents are in most cases discharged directly or indirectly into the river. A total of four different sampling sites were selected from the NCR. They are Aluu, Iwofe, Elibrada and Choba Bridge. Surface water was sampled randomly on four occasions for the determination of the following Physicochemical parameters: pH, dissolved oxygen (DO), biochemical oxygen demand (BOD), total dissolved Solid (TDS), conductivity, salinity, turbidity, nitrate, phosphate, total hardness, chloride and sulphate

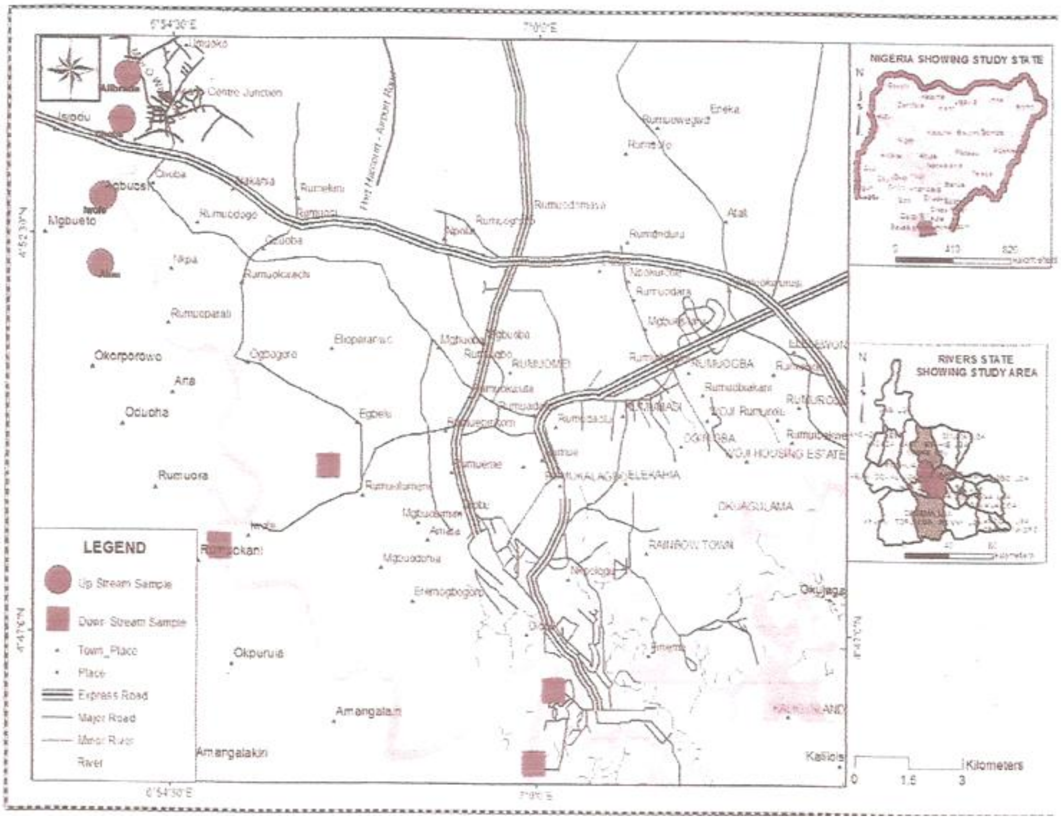

Figure 1: Map of New Calabar River showing sampling sites

Collection of surface water

The plastic bottles for the collection of surface water sample were washed with water and rinsed with nitric acid. The surface water samples were collected in 2 liter capacity plastic bottles with screw cap at 2cm depth and 5ml of concentrated nitric (HNO_3) acid was added to preserve the metals. The water sample for biochemical oxygen demand and dissolved oxygen were collected differently with great care in two sets of 250ml glass stoppered reagent bottles and wrapped in dark polyethylene bags to prevent light which can lead to production of DO. The sample was fixed with Winkler I and II reagents.

Determination of Physicochemical Parameters

Determination of pH

The water sample was collected into a 1000ml flask and the pH meter was used to determine the pH of the water *in situ*. Measurements were taken four times and the average determined [9].

Determination of DO

Winkler method was used to measure dissolved oxygen. 5m1 manganese sulphate, 5ml alkali iodide azide, 1ml concentrated sulphuric acid (H_2SO_4) and 1ml of starch indicator was added to an aliquot of 100ml which was withdrawn from the treated water sample and stirred. The solution was then titrated with standard 0.025m sodium thiosuiphate ($Na_2S_2O_3.5H_2O$) until the blue colour changes to colourless indicating end point [10]. The volume of the sodium thiosulphate ($Na_2S_2O_3.5H_2O$) used was recorded and calculated. DO (mg/l) = volume of 0.025M $Na_2S_2O_3.5H_2O$ used.

Determination of biochemical oxygen demand (BOD)

The water samples were first incubated in the dark for five days. DO was determined by Winkler's method. Two DO determinations were carried out, one before incubation and the other, after incubation respectively. The BOD was subsequently calculated based on the difference in the two DO levels.

Determination of chloride (Cl^-) ion

This was determined by placing l00ml of the water sample in a 250m1 beaker. The pH was adjusted to the range of 7-10 by gradually adding H_2SO_4, 1ml of K_2CrO_4 was added as indicator and the solution was titrated with 0.1 4M silver nitrate to give a pinkish yellow end point.

Determination of turbidity

This was measured with the aid of a turbidimeter GLI model MG 99701-0. The probe was immersed in the water sample and the reading taken from the digital display on the instrument.

Determination of nitrate (NO_3^-) (Colorimetric method)

Ten (10) cm^3 of the water sample was transferred into 25ml volumetric flask. Then 2m1 of Brucine reagent (dimethoxystrychnine-$C_{23}H_{26}O_4N_2.2H_2O$) was added, followed by the addition of 100ml of concentrated H_2SO_4. The content was mixed for about 30 seconds and allowed to stand for 30 minutes. The flask was air cooled for 15 minutes, made up to the mark, and the absorbance was measured by portable datalogying spectrophotometer model DR12023 at the wavelength of 470nm. Standard nitrate solution was prepared by dissolving 0.8g of KNO_3 in 500cm^3 of distilled water. 0.5cm_3 of chloroform was added in order to preserve it. Aliquots having concentrations range of 0.01-2.OM of (NO_3^-) were prepared from stock solution and used to obtain a calibration curve. The absorbance obtained for each sample was compared to the calibration curve and the concentration of nitrate in each sample was obtained.

Determination of sulphate (SO_4^{2-}) (Turbid metric Method)

10ml of the water sample was measured into 50ml volumetric flask and 5ml of distilled water was added. 1 ml of gelatinous reagent (Gum acacia) was added and made up to the mark with distilled water that formed barium sulphate turbidity. The content was thoroughly mixed and allowed to stand for 30 minutes. The optical density (OD) corresponding to the absorbance of the barium sulphate was measured spectrophotometrically using a HACH DR/20 10 portable datalogying spectrophotometer at a wavelength of 420nm. Reading was taken at intervals of 30 seconds over a period of 4 minutes and the maximum reading resolved. A calibration curve was prepared using analytical grade anhydrous potassium sulphate (K_2SO_4) that covered the range of 0.01- 1 .6mg/l SO_4^{2-}. From the calibration plot, the level of sulphate ion equivalent to the observed optical densities (absorbance of the test and blank solution) were read off and the level of sulphate (SO_4^{2-}) ion in the sample obtained.

Determination of conductivity

This was measured with conductivity Scan Meter model 1560. The probe of the meter was rinsed with demineralised water, for each measurement. The probe was thereafter immersed in the sample contained in a clean beaker and the instrument switched on for a stabilized digital display value expressed in µs/cm.

Determination of total dissolved solid (TDS)

The total dissolved solid (TDS) were obtained by filtration and evaporation methods. Filter paper was used to filter the sample and the filtrate was fried in an oven at 190°C. A desiccator contain silica gel was used to cool the dish and both the dish and the content was weighted to record the increase in weight which represents the TDS of the sample [11].

Determination of salinity

Salinity was determined by titrating aliquot of $AgNO_3$(aq) Solution. Potassium Chromate was used as an indicator.

Total Hardness (Calcium hardness)

l ml of buffer solution was added into 50ml water of each sample in addition with 1-2 drops of indicator. This prepared solution was titrated against EDTA solution. The pink real colour of solution was turned into blue showing the completion of titration. The hardness was calculated.

Results and Discussion

Physicochemical Parameters of Surface Water Samples analyzed.

The results of the physical parameters obtained from Surface Water samples are presented in table 1 below.

Table 1: Physicochemical Parameters of Surface Water Samples from New Calabar River (Means ± SD) of 4 Determinations

Parameter	**Location**					
	Aluu (ARAC)	**Iwofe**	**Elibrada**	**Choba Bridge**	**Mean±SD**	**WHO Standard**
pH	7.60	7.45	7.45	7.35	7.46±0.089	6.5-8.5
Conductivity (μS/cm)	1780.5	1998.52	2820.23	8790.40	3847.41±2880.05	500
TDS (mg/l)	890.5	9990.02	1410.18	4395.68	4171.60±3615.77	250-500
Turbidity (NTU)	2.20	6.80	2.30	7.85	4.79±2.56	5
Salinity (mg/l)	746.50	5994.45	842.38	2659.65	2560.75±2123.93	200-250
DO (mg/l)	6.35	5.53	5.98	5.33	5.80±0.50	5-10
BOD (mg/l)	4.65	11.10	6.44	15.75	9.49±4.31	4
SO_4^{2-}(mg/l)	4.56	57.77	4.16	23.43	22.48±21.81	250-500
NO_3 (mg/l)	10.72	45.68	8.88	16.27	20.39±14.85	10
PO_4^{3-}(mg/l)	1.01	0.90	0.52	0.87	0.83±0.18	0.5
Cl^-(mg/l)	453.5	3592.03	572.61	1612.48	1557.66±1258.09	4
Total Hardness (mg/l)	35.08	47.06	36.50	42.50	40.29±4.80	200

Table 1 presents the physicochemical parameters of Surface water Samples from the various sample locations, with their mean concentration and the World Health Organisation standard.

pH

The mean level of the pH was 7.46±0.089. However, the pH from the various sample locations showed that Aluu was 7.60, Iwofe (7.4), Elibrada (7.45) and Choba bridge was 7.35. These pH levels and their mean were within the permissible limit set by WHO. From the results, Aluu surface water had the highest pH of 7.60 but that still falls within the limit of the World Health Organisation. The levels indicated that the surface water samples are within pH range and in agreement with reports by other Scholars [2], who reported a pH of 7.4. This work also correlate work by Chinedu et al. [12], they had a pH range of 6.2 ± 0.52 to 7.2 ± 0.52 on surface water around Ota, South West Nigeria. At pH of approximately 4.0 or below and pH of 11 or above, most species die [13].

Conductivity

The conductivity from the different locations were excessively high. The mean level was 3847.1 ± 2880.05 µs/cm while the conductivity from the various locations range between 1780.50 and 8790.40µs/cm. These results were higher than the WHO permissible limit of 500 µs/cm. This study is far above reports by Edori and Kpee [14] on water samples in Port Harcourt. High conductivity could be attributed to the iron and metal work in some industries close to the river.

Total Dissolved Solid

The mean concentration of TDS obtained in the study was 4171.60 ± 3615.77 mg/l. However, the TDS obtained from the locations ranged from 890.5 to 9990.02mg/l. The lowest TDS was recorded for Aluu while the highest was Iwofe. This TDS values and their mean are above the permissible limit of 200 to 500mg/l set by WHO. The high TDS obtained in the work especially at the Iwofe location could probably be attributed to volume of wastes generated from the numerous companies around these locations. Alabaster and Lloyd [15] suggested that excessive concentrations of suspended and dissolved solid might be harmful to aquatic organism, because they decrease water quality, inhibit photosynthetic processes and eventually lead to increase in bottom sediment and decreases of water depth.

Turbidity

The turbidity obtained from the study range between 2.20 and 7.85NTU while the mean was 4.79±2.56. The lowest turbidity level was recorded from Aluu and the highest from Choba. Results reveals that the turbidity level of all the sampled locations were within the WHO permissible limit. This result is in contrast with the level reported a mean turbidity of 0.2± 0.00 NTU at Omoku. This results is an indication of high rate of anthropogenic activity (fishing, farming etc.) showing that more silt /mud are been washed into the river. The greater the turbidity, the higher the risk of gastrointestinal diseases. High turbidity reduces photosynthetic activities in the ecosystem due to reduce light penetration [2].

Salinity

The sanity values of the surface water varied from site to site. Higher salinity value was recorded in Iwofe (5994.45mg/l) than that of Choba (2659.65mg/l), Elibrada (842.38mg/l) and AIuu (746.50 mg/I). The mean salinity was 2560.75±2123.93. The WHO recommended limit for salinity in surface water is between 200 and 250mg/l and from observation, results obtained from this work are more than the limit set by WHO. Dienye and Worke [3], results were at variance with the one obtained in this study. The high level of salinity could be attributed to the level of organic and non-organic materials on the water environment which are generated from industrial activities around these locations.

Level of Chloride (Cl^-) in surface water

The levels of chloride in mg/I from the various locations were Iwofe (453.5), Elibrada (3592.03), Choba (572.6) and Choba Bridge (1612.48) while the mean was 1557.66±1258.09. The results revealed that the concentrations obtained from the various locations were far above the WHO standard of 4mg/l indicating that the water from NCR is excessively polluted with chloride. The study also showed that the chloride concentration at Iwofe location was higher than others. This indicates that Iwofe location is concentrated with effluent from industries and companies operating in the area.

Dissolved Oxygen in surface water

The concentration of dissolved oxygen in mg/I in Aluu was 6.35, Iwofe (5.55), Elibrada (5.98) and that of Choba bridge was 5.33. Although the DO level from the Iwofe location was slightly higher than the levels of DO obtained from Aluu, Elibrada and Choba bridge. The DO from all the locations were within WHO permissible limit. These levels of DO are suitable for aquatic life since dissolved oxygen is essential to maintain the higher form of biological life. The mean level of DO was 5.8 ± 0.50. The level of DO obtained in this study disagrees with those observed in different boreholes near, Abattoirs in Port Harcourt recorded by Edori and Kpee [14].

Biochemical Oxygen Demand levels in surface water

The concentrations (mg/l) of Biochemical oxygen demand obtained were Aluu (4.65), Iwofe (11.10 mg/I), Elibrada (6.44) and Choba bridge (15.75). The BOD of the various stations were more than the approved limit of 4mg/l by WHO. Increased BOD in this study implies that the water contains a lot of organic matter.

The BOD recorded from Aluu was in agreement with WHO permissible limit. The BOD from this study has a mean value of 9.49 ± 4.32 which disagrees with the observed level of BOD from the study at Buguma Creek by Makinde et al. The BOD values from Iwofe, Aluu and Choba bridge exceeded the permissible limit according to the ranking of World Health Organization [16], which emphasizes on water bodies with BOD levels between 1 .0 mg/l and 2.0mg/; as clean and unpolluted, 3.0mg/l as fairly clean, 5 .0mg/I as bad and polluted. The BOD of a water body is responsible for its odour and taste.

Sulphate (SO_4^{2-}) ion in surface water

The formation of sulphate in water is from the decomposition of various substances that contain Sulphur. Sulphate ions SO_4^{2-} occur naturally in most water. The concentrations of SO_4^{2-} were Aluu (4.56mg/I), Iwofe (57.77mg/I), Elibrada (4.1 6mg/I) and Choba bridge (23.43mg/l). The mean concentration obtained for sulphate was 22.48±21.81. The level of sulphate obtained in this work was low compared with WHO limit (250-500mg/I). The geological formation of the soil type as well as the leaching and penetration of waste through the soil strata is responsible for the presence of sulphate in water in most cases.

Level of Nitrate in surface water

The concentration of nitrate obtained from Aluu location was 10.72mg/I, Iwofe was 45.68mg/l, Elibrada was 8.88mg/I and from Choba bridge was 16.27mg/I. The mean concentration was 20.39 ± 14.85 which is above the permissible limit of 10mg/l set by WHO. The level of nitrate obtained for Iwofe (45.68) and Choba bridge (16.27mg/I) locations were higher than WHO permissible limit of 10mg/l. The implication of this is that water from Iwofe and Choba bridge locations contain high level of oxidized organic matter which appears in the form of soluble anions such as nitrates. The high level of nitrate in Iwofe and Choba bridge can be attributed to the existence of decayed organic matter and water runoff from farmland and leaking septic tank.

Level Phosphate in surface water

The concentration of phosphate obtained from the four locations in NCR ranged from 0.52 to 1.01mg/l with mean concentration of 0.83±0.18. From the sudy, the highest concentration of phosphate was obtained from the Aluu location while the lowest was from Elibrada. The WHO recommended that the set limit for phosphate in drinking water is 0.5mg/l. The Aluu, Iwofe, and Choba locations were more than the recommended limit set by WHO. This implies that the NCR is polluted with phosphate.

Level of Total Hardness in surface water

At the Iwofe location, the obtained total hardness was 47.06mg/l, Aluu (35.08mg/l), Elibrada (36.50mg/l) and Choba bridge (42.50mg/l). The mean concentration of total hardness was 40.29±4.80.The recommmended limit of total hardness in drinking water by WHO is 200mg/l. The NCR is safe with regard to total hardness as the obtained values from the study are all within the recommended limit.

Conclusion

The water quality with particular reference to the physicochemical parameters of the NCR was carried out to ascertain the quality of the water. The results revealed that the water is not safe for domestic purposes. This is because of the twelves parameters investigated, only three were found to have concentrations wthin the limit set by WHO. The water is not only unsafe for domestic purpose but it has been observed that some of the aquatic habitats that were noticed to be common in the river are no longer available. This call for caution on the part of the government and the companies operatiing within the vicinity of the river. On the part of the operating companies, there is the need to properly treat the generated wastes before discharging them and the government should see as a matter of urgency to conduct an environmental audit on the NCR.

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