3.2.6 HEAVY METAL DETERMINATION

The concentration of heavy metals present in the different water samples was determined using Atomic Adsorption Spectrophotometer (AAS). (SOLAAR 969 UNICAM SERIES, using air acetylene flame).

3.2.7 TEMPERATURE

Temperature was noted by thermometric method at the sampling using portable calibrated Mercury thermometer in the Multi-Parameter Meter.

3.2.8 ELECTRICAL CONDUCTIVITY

The ability of the aqueous solution to convey current was determined using the Conductivity Meter in the Multi-Parameter Meter.

3.2.9 BIOLOGICAL OXYGEN DEMAND (BOD)

The samples were incubated for 5days at 20^{o}C in the dark, the reduction in dissolved oxygen concentration during the incubation period yields a measure of the BOD.

3.2.10 COLOUR

Colour was determined by using GENESYS-10VIS Spectrophotometer, based on the difference between the sample colour and the water colour.
Colour of water in mg/l PtCo = (Sample Colour – Water Colour)

3.3 STATISTICAL ANALYSIS OF DATA

To assess the variation of the overall water quality along the river, Water Quality Index (WQI) modelling was done on twenty-five physico chemical properties of the water samples in March, May, and July, 2014. WQI was computed for each sampling period using the following approach;

3.3.1 DETERMINATION OF WEIGHTAGE

In calculating WQI, the Weightage of each of the parameters identified was first ascertained. Parameters with higher allowable limit are less toxic because they cannot change surface water quality even when they are in large amount. Therefore, the weightage of tested parameters has an inverse relationship with the allowable limit. Hence

$$W_n = \frac{K}{S_n} \quad (1)$$

where:
Wn = Tested Parameter Unit Weight
Sn = WHO Standard Values
K = Constant of proportionality

$$K = \frac{1}{\sum_{i=1}^{s} \frac{1}{S_n}} \quad (2)$$

3.3.2 QUALITY RATING COMPUTATION

Rating scale was assembled for set of values of each parameter. This rating ranged from 0 – 100 and was shared in intervals of five. The rating q_n= 0 indicates severe pollution (the tested parameter indices surpasses the maximum allowable limit. Conversely, q_n= 100 is an indication that parameter indices available in the water has desirable values. Other ratings (q_n= 40, q_n= 60 and q_n= 80) are within these extremes. These values represent excessive pollution, moderate pollution and slightly less pollution respectively. This is the modified version of the rating scale; it is calculated as follows [13, 14]:

$$q_n = \frac{100(V_n - V_{io})}{(S_n - V_{io})} \tag{3}$$

where:
q_n = Quality rating or sun index
V_n= Test result for each parameter tested
S_n= Standard value of each parameter
V_{io}= ideal value of selected parameters tested (in pure water V_{io}= 0 for all parameters tested except pH and dissolved oxygen which is 7.0 and 14.6 respectively.

The resulting value is multiplied by a weightage factor which has significance to the water quality. The resulting sums are added to obtain one WQI for the water. It is a mathematical approach for the calculation of a unit number from various test results. The Water Quality Index calculated from the results, is a representation of the level of water quality in any given water body. The steps below were followed in evaluation of WQI in the river:

i. The weightage unit (W_n) were determined for all tested parameters and added to get $\sum W_n$
ii. The quality rating of all parameters tested were added to get $\sum q_n$
iii. The index W_n*q_n was calculated for each parameter tested and summed up to obtain $\sum W_n.q_n$
iv. Mass balance equation was used to compute WQI for each water sample $\frac{\sum W_n.q_n}{W_n}$
v. Water Quality Index (WQI) = 100-Z was used to represent the level of water quality.

Also, factor analysis using Principal Component Analysis (PCA) for the months of March, May and July 2014 was used to assess that all the water quality parameters used for the analysis contributes reasonably to the overall variation in the quality of the river water. The analysis was carried out using statistical software, SPSS version 16.0 (statistical package for the social sciences).

4.0 DISCUSSION OF RESULTS

The physcio-chemical analysis results of the 25 selected parameters are presented in Table 2 and were compared with WHO and Federal ministry of Environment Standards. WQI was computed from the values in Table 2; the results indicate a serious level of pollution occasioned by the discharge of poorly treated brewery effluent into Ikpoba River. WQI computed for station one in March, 2014 was as high as -5429792.89; this is an indication that brewery effluent is highly polluted and when released in its raw state into the river, the consequences is high degree of water pollution as experienced in all the stations from which water samples were collected. The bar chart showing water quality index (WQI) with sampling stations for the period under investigation are shown in Figures 2, 3 and 4 respectively.

Pollution levels were observed to be higher at the point source of brewery effluent and at the discharge point compared to upstream and downstream locations of the Ikpoba River. This is deduced from the levels of the water quality parameter at the point source of effluent being higher than at the discharge points and in turn the discharge points correspondingly higher than the upstream and downstream locations respectively. The brewery effluent at point source had high values of COD, EC, temperature, TSS, TDS, Cl^-, SO_4, and HCO_3 which experienced considerable reduction at the discharge point where the effluent mixes with the river as a result of dilution principle. The values at the upstream and downstream locations were lower as a result of dilution. For TSS, a significant rise was noticed throughout the sampling periods from the upstream to the downstream locations. This can be explained from the movement of brewery effluents with high TSS levels into the river which experiences differential sedimentation as we move down the reach of the river. The levels of TSS during the rainy months (May and July, 2014) were generally lower compared to the dry month of March, 2014; this is attributable to the solubility of the solids discharged during rainy season.

Table 2: Comparison of the overall range of the water quality of Ikpoba River (March –July, 2014) with some water quality standards

Parameters	Range of parameter values Ikpoba river	Water quality standards	
		WHO	FMNEV
Temperature (^oC)	25.4 – 37.1		<40
pH	6.2 -10.6	7-8.5	6-9
EC (µS/cm)	30 -1654		400
TDS (mg/l)	20 – 827	100	2000
TSS (mg/l)	5.2 -142.5		30
Turbidity (NTU)	8 – 71		
Cl^- (mg/l)	20.7 – 141.8		200
PO_3^{4-} (mg/l)	0.15 – 9.40		
NO_3^- (mg/)	0.02 – 2.63	50	
Cd (mg/l)	0.002 – 0.102	0.003	<1
Zn (mg/l)	0.06 – 0.14	0.01	<1
Pb (mg/l)	0.0003 – 0.103	0.01	<1
Ni (mg/l)	0.0003 – 0.213	0.02	
Cu (mg/l)	0.001 – 0.18		
Ca^{2+} (mg/l)	0.45 – 14.41		
Salinity (g/l)	0.0018 – 0.578		
DO (mg/l)	4.0 – 6.90		
BOD_5 (mg/l)	2.0 – 5.7		50
COD (mg/l)	28.8 – 242.4	10-20	150
THC	0.46 -5.70		
Mg(mg/l)	0.005 – 9.51		
Na (mg/l)	0.50 – 53.10		
SO_4	0.68 – 34.75		
V(mg/l)	0.003 – 0.27		
Fe(mg/l)	0.59 -6.74		

The levels of these parameters at point source when compared with the discharge standards as stated by WHO; pH, COD, turbidity, TSS and PO_3^{4-} were found to be much higher than discharge standard. At the upstream and downstream locations, there was reduction in the parameters values which is due to dilution. The pH values of the brewery effluent at point source range from 9.8 – 10.6 which were the highest compared to the discharge point which range from 6.9 – 8.6. The high pH values of the brewery effluent at the point source which exceeded the WHO limit are not surprising since the brewery process requires use of disinfectants and batch discharging of caustic cleaning solutions or basic detergent for the cleaning stage. At the discharge point, pH values were within the permissible limits of 6.5 – 9.5 by WHO discharge standards. The upstream pH values were slightly higher than the corresponding downstream locations, however the average pH values of the upstream and downstream stations of the Ikpoba River during the rainy months (May and July, 2014) were higher than the corresponding end of dry season.

At the discharge point of brewery effluent, dissolved oxygen levels were much lower than corresponding levels for either upstream or downstream sampling points with a much higher chemical oxygen demand than corresponding levels for both upstream and downstream locations. The DO levels at the point source of brewery effluent ranged from 4.0 to 5.0mg/l and the discharge point ranged from 4.5 to 5.5mg/l. the DO levels at the upstream ranged from 5.2 – 6.5mg/l while the average DO of downstream location is 6.2mg/l. The DO values obtained at the point source is an indication that the brewery effluents contain a high organic load of matter that could have consumed the available dissolved oxygen. The COD at the point source ranged from 196.0 to 242.4mg/l while it ranged 171.2-182.2mg/l at the discharge, upstream and downstream points; indicating that the brewery effluent at the point source would require more oxygen due to high oxygen demanding waste than at the discharge, upstream and downstream points. The average level of ammonium nitrogen in the brewery effluent at point source and the discharge point during transition from dry to rainy seasons ranged from 0.98 to 2.63mg/l and 0.12 to 1.60mg/l respectively. The presence of ammonia concentrations in the effluent has its origin from the proteins and chitins load contained in the brewery waste [15]. Apart from the high organic content of brewery effluent, spent wash generated from the fermentation step also contains nutrients in the form nitrogen. Spent wash is the dark brown distillery wastewater generated during the fermentation step of beer production [15].

The overall turbidity of the brewery effluent ranging from 17-71NTU indicates the quantity of TSS in it, particularly at such high solid concentration (142.5mg/l) in the dry month of March. Turbidity does not directly correlate with suspended concentration because colour can sometimes interfere with its measurement; none the less it affords a relative indication of suspended solid levels [16]. The salinity level of the river at upstream locations during the end of the dry season of March 2014 was 0.02g/l, and 0.027g/l and 0.036g/l during the rainy season of May and July, 2014. The salinity level was raised to 0.027g/l, 0.032g/l and 0.045g/l at the downstream locations during both seasons. The observed increases were due to flow of brewery effluent discharge with high alkalinity levels at all instances with corresponding drops from downstream locations resulting from dilution along the reach of the river. Zn, Pb, Cd, and Ph in all the locations of investigations far exceeded the WHO allowable limits during the period of study. Environmental concern associated with the Ph, Cd and Pb are centred on the ecological simulation of algae growth in the river to water poisoning and undesirable depletion of DO in the river [17, 18].

Figures 2, 3 and 4 revealed that higher level of water pollution was experienced in the month of March (dry season) as compared to May and July (wet season). The lower level of pollution experienced in the month of May and July is due completely to the high volume of water present in the river occasioned by seasonal variation (raining season). The high volume of water tends to dilute the concentration of the effluent as the distance away from the point source of pollution increases [19, 20]. Also, the high volume of water promotes increased steady rate of flow and boost the self-replenishing and purification effects of the river body [21, 22].

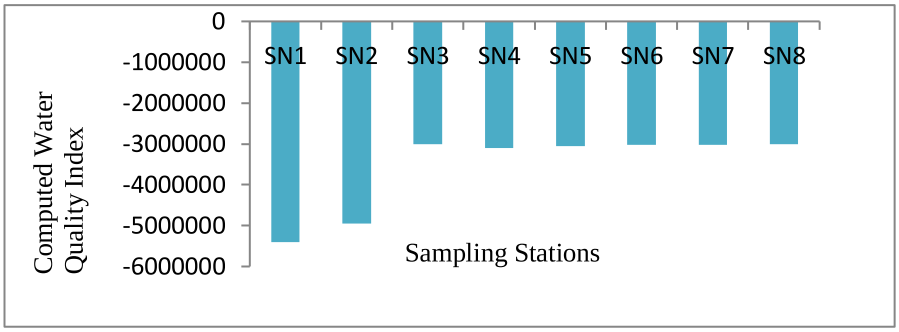

Figure 2 Variation of WQI with sampling stations for the month of March, 2014

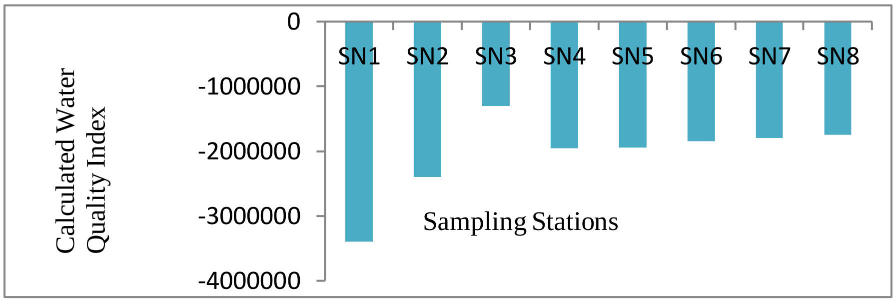

Figure 3 Variation of water quality index with sampling stations for the month of May, 2014

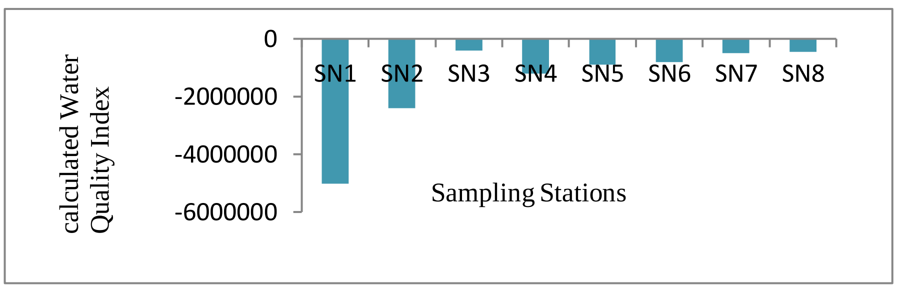

Figure 4 Variation of water quality index with sampling stations for the month of July, 2014

Since the overall status of the river is characterized by high level of pollution occasioned by the discharge of poorly treated brewery effluent, then it is important to establish the contributions of each physcio-chemical parameters of the river water that was investigated. This is to distinguish the parameters that promote high level of contamination from those that contribute minimal pollution. This was achieved by subjecting the test parameters (25) to statistical analysis using Principal Component Analysis (PCA). This method of PCA was employed to perform the analysis and the anti-mage correlation matrix was used to ascertain the viability of factors analysis in explaining the correlation of the physcio-chemical properties. The results showed that the entire off-diagonal matrix is less than unity (one) hence the factor analysis is adequate for the analysis. PCA was also utilized in extraction analysis; this is to determine how well the factors explain the variation in the physcio-chemical properties with distance along the river using the total variance. The extraction solution using PCA reveals that the 25 physcio-chemical properties can only be grouped into three component matrix as seen in the solution of the initial eigenvalues. The results are show in Tables 3-5.

Table 3: Extraction using principal component analysis (March, 2014)

Total Variance Explained									
Component	Initial Eigenvalues			Extraction sum of squared loadings			Rotation sum of squared loadings		
	Total	% Var.	% Cum.	Total	% Var.	% Cum.	Total	% Var.	% Cum.
1	20.92	83.67	83.67	20.92	83.67	83.67	10.92	43.68	43.68
2	2.08	8.34	92.01	2.08	8.34	92.00	8.02	32.09	75.76
3	1.00	4.01	96.01	1.00	4.01	96.01	5.06	20.25	96.01
4	0.82	3.27	99.28						
5	0.17	0.69	99.97						
6	0.01	0.02	99.99						
7	0.002	0.01	100.00						
8	3E-15	1E-14	100.00						
9	9E-16	4E-15	100.00						
10	8E-16	3E-15	100.00						
11	6E-16	2E-15	100.00						
12	5E-16	2E-15	100.00						
13	4E-16	1E-15	100.00						
14	3E-16	1E-15	100.00						
15	2E-16	1E-15	100.00						
16	1E-16	5E-16	100.00						
17	5E-17	2E-16	100.00						
18	-3E-17	-1E-16	100.00						
19	-2E-16	-7E-16	100.00						
20	-3E-16	-9E-16	100.00						
21	-4E-16	-1E-15	100.00						
22	-5E-16	-2E-15	100.00						
23	6E-16	-2E-15	100.00						
24	-7E-16	-3E-15	100.00						
25	-9E-16	-4E-15	100.00						

Extraction Method: Principal Component Analysis

Table 4: Extraction using principal component analysis (May, 2014)

Total Variance Explained									
Component	Initial Eigenvalues			Extraction sum of squared loadings			Rotation sum of squared loadings		
	Total	% Var.	% Cum.	Total	% Var.	% Cum.	Total	% Var.	% Cum.
1	21.40	85.59	85.59	21.40	85.59	85.59	16.05	64.18	64.18
2	1.60	6.37	91.96	1.59	6.37	91.96	6.38	25.54	89.71
3	1.08	4.33	96.29	1.08	4.33	96.29	1.64	6.57	96.29
4	0.79	3.15	99.44						
5	0.13	0.52	99.961						
6	0.08	0.03	99.99						
7	0.02	0.01	100.00						
8	1.7E-15	6.9E-15	100.00						
9	8.4E-16	3.4E-15	100.00						
10	8.7E-16	2.8E-15	100.00						
11	4.8E16	1.9E-15	100.00						
12	4.2E-16	1.7E-15	100.00						
13	2.4E-16	9.7E-16	100.00						
14	1.1E-16	4.3E-16	100.00						
15	3.2E-17	1.3E-16	100.00						
16	-3.3E-17	1.3E-16	100.00						
17	-8.4E-17	-3.4E-16	100.00						
18	-1.3E-16	-5.2E-16	100.00						
19	-2.7E-16	-1.1E-15	100.00						
20	-4.1E-16	-1.6E-15	100.00						
21	-5.5E-16	-2.2E-15	100.00						

22	-5.7E-16	-2.3E-15	100.00
23	-6.8E-16	-2.7E-15	100.00
24	-7.1E-16	-2.8E-15	100.00
25	-1.5E-15	-6.1E-15	100.00
Extraction Method: Principal Component Analysis			

Factors with eigenvalues greater than one represent the number of factors needed to describe the underlying dimensions of the effect of brewery effluents on the river water quality. These are the factors that contributes adequate amount to the variation in the physcio-chemical properties of the water samples collected at different points along the river. The eigenvalues is used as a cut off in factors analysis since it the sum of the squared factors loadings of all variables. Factors with eigenvalues less than one means that such factors such factor do not have any influence on the overall issue under study. The results obtained from the factor analysis are shown in Figures 5, 6 and 7 indicates that there are three (3) component factors with eigenvalues greater than unity. These are the component factors with the highest influence on the river quality.

Table 5: Extraction using principal component analysis (July, 2014)

Total Variance Explained									
Component	Initial Eigenvalues			Extraction sum of squared loadings			Rotation sum of squared loadings		
	Total	% Var.	% Cum.	Total	% Var.	% Cum.	Total	% Var.	% Cum.
1	20.26	81.06	81.06	20.26	81.06	81.06	13.84	55.37	55.37
2	2.77	11.02	92.08	2.76	11.02	92.08	8.33	33.30	8.66
3	1.43	5.71	97.79	1.43	5.71	97.79	2.28	9.13	97.79
4	0.42	1.67	99.46						
5	0.13	0.51	99.97						
6	0.001	0.03	99.99						
7	0.002	0.006	100.00						
8	1.1E-15	4.5E-15	100.00						
9	8.2E-16	3.3E-15	100.00						
10	6.3E-16	2.5E-15	100.00						
11	5.6E-16	2.2E-15	100.00						
12	4.2E-16	1.7E-15	100.00						
13	3.3E-16	1.3E-15	100.00						
14	2.0E-16	8.1E-16	100.00						
15	1.3E-16	5.2E-16	100.00						
16	6.4E-17	2.6E-16	100.00						
17	-4.9E-17	-2.0E-16	100.00						
18	-2.0E-16	-8.1E-16	100.00						
19	-2.8E-16	-1.1E-15	100.00						
20	-3.0E-16	-1.2E-15	100.00						
21	-4.3E-16	-1.7E-15	100.00						
22	-5.6E-16	-2.3E-15	100.00						
23	-8.4E-16	-3.6E-15	100.00						
24	-1.0E-15	-4.1E-15	100.00						
25	-2.9E-15	-1.2E-15	100.00						
Extraction Method: Principal Component Analysis									

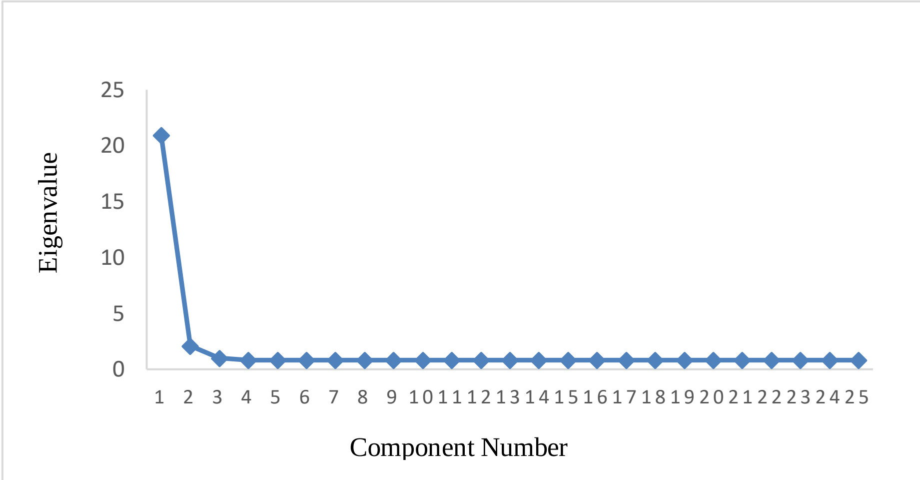

Figure 5: Screen plot showing component factors with highest influence (March, 2014)

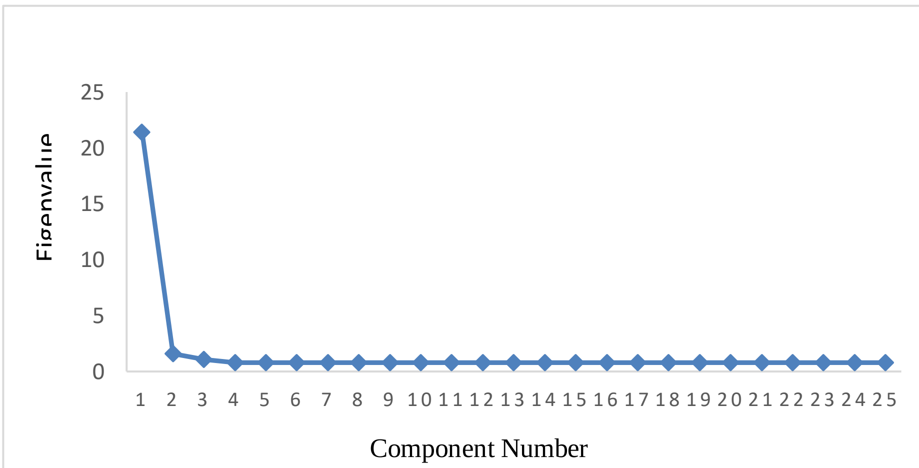

Figure 6: Scree plot showing component factors with highest influence (May, 2014)

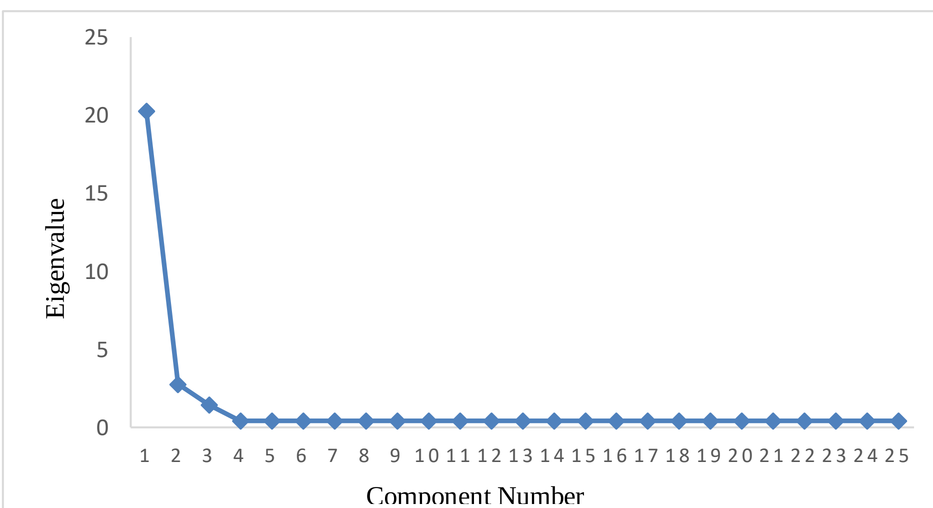

Figure 7: Scree plot showing component factors with highest influence (July, 2014)

From the results of the scree plots, it is clear that three component factors possess very strong influence on the overall quality of the river water. To find the variables that make up each of the component factors, factor loadings was checked and the best favoured variable was selected for component factors. The results of the factor loadings are presented in Table 6, 7 and 8.

Table 6: Makeup of the component factors (March, 2014)

Variables		Component Factors		
Variable Code	Variable Name	1	2	3
X_1	pH	0.980		
X_2	Nitrate	0.904		
X_3	Electrical Conductivity	0.924		
X_4	Turbidity	0.980		
X_5	Dissolved Oxygen		0.648	
X_6	TDS	0.925		
X_7	Sodium	0.985		
X_8	Lead	0.922		
X_9	Sulphates	0.991		
X_{10}	Zinc	0.898		
X_{11}	Copper	0.987		
X_{12}	Chloride	0.995		
X_{13}	Iron	0.933		
X_{14}	BOD_5	0.576		
X_{15}	COD	0.980		
X_{16}	HCO_3	0.983		
X_{17}	TSS	0.757		
X_{18}	Ammonia	0.882		
X_{19}	Nitrite	0.946		
X_{20}	Cadmium	0.938		
X_{21}	Nickel	0.956		
X_{22}	THC	0.949		
X_{23}	Phosphate	0.970		
X_{24}	Magnesium	0.759		
X_{25}	Calcium	0.907		

The results presented in Tables 6 reveals that the first component factor is most highly correlated with; pH, nitrates, EC, turbidity, TDS, sodium, lead, sulphate, zinc, copper, chlorine, iron, BOD, COD, bicarbonate, TSS, ammonia, nitrite, cadmium, nickel, THC, phosphate, magnesium and calcium. Chloride has the strongest influence with a magnitude of 0.995. The second component is most highly correlated with dissolved oxygen. The results also show that chloride, COD, sulphate, copper, sodium, and carbonate are the most important variables affecting the quality of the river water in March, 2014.

Table 7: Makeup of the component factors (May, 2014)

Variables		Component Factors		
Variable Code	Variable Name	1	2	3
X_1	pH	0.963		
X_2	Nitrate	0.991		
X_3	Electrical Conductivity	0.946		
X_4	Turbidity	0.962		
X_5	Dissolved Oxygen		0.531	
X_6	TDS	0.944		
X_7	Sodium	0.982		
X_8	Lead	0.986		
X_9	Sulphates	0.975		
X_{10}	Zinc	0.987		
X_{11}	Copper	0.980		
X_{12}	Chloride	0.895		
X_{13}	Iron	0.942		
X_{14}	BOD_5		0.725	
X_{15}	COD	0.936		
X_{16}	HCO_3	0.996		
X_{17}	TSS		0.572	
X_{18}	Ammonia	0.991		
X_{19}	Nitrite	0.993		
X_{20}	Cadmium	0.918		
X_{21}	Nickel	0.921		
X_{22}	THC	0.997		
X_{23}	Phosphate	0.938		
X_{24}	Magnesium	0.986		
X_{25}	Calcium	0.953		

In Table 7, it was observed that the first component factor is most likely correlated with; pH, nitrate, EC, turbidity, TDS, sodium, lead, sulphates, zinc, copper, chloride, iron, COD, bicarbonate, ammonia, nitrite, cadmium, nickel, THC, phosphate, magnesium and calcium. Total Hydrogen Content (THC) has the strongest influence with a magnitude of 0.997. The second component factor is most likely to correlate with Total Suspended Solids (TSS), dissolved oxygen and Biochemical Oxygen Demand (BOD). It was also noticed that nitrate, sodium, lead, copper, zinc, ammonia, nitrite, magnesium, THC, and carbonate are the most important variables affecting the quality of the river water in May, 2014.

Table 8 shows that the first component factor is most likely correlated with pH, nitrate, EC, turbidity, TDS, ammonia, nitrite, cadmium, nickel, THC, phosphate, magnesium, and calcium. The second component factor is most highly correlated with BOD. It was also observed from the results that dissolved oxygen do not have any influence on the quality of water in the month of July, 2014. The most important variables affecting the quality of the water in the river in July, 2014 are; turbidity, zinc, copper and phosphate.

Table 8: Makeup of the component factors (July, 2014)

Variables		Component Factors		
Variable Code	Variable Name	1	2	3
X_1	pH	0.750		
X_2	Nitrate	0.831		
X_3	Electrical Conductivity	0.905		
X_4	Turbidity	0.987		
X_5	Dissolved Oxygen			
X_6	TDS	0.909		
X_7	Sodium	0.976		
X_8	Lead	0.975		
X_9	Sulphates	0.946		
X_{10}	Zinc	0.992		
X_{11}	Copper	0.991		
X_{12}	Chloride	0.939		
X_{13}	Iron	0.697		
X_{14}	BOD_5		0.880	
X_{15}	COD	0.954		
X_{16}	HCO_3	0.979		
X_{17}	TSS	0.652		
X_{18}	Ammonia	0.978		
X_{19}	Nitrite	0.863		
X_{20}	Cadmium	0.923		
X_{21}	Nickel	0.880		
X_{22}	THC	0.960		
X_{23}	Phosphate	0.996		
X_{24}	Magnesium	0.925		
X_{25}	Calcium	0.956		

Evaluation of the results in Tables 6-8 shows that the only reoccurring parameter is copper hence it is concluded that copper is the only component factor that influences the river water quality throughout the period under study. Therefore, it is strongly recommended that any proposed treatment method must be targeted at the removal of copper in addition to other factors of high contributory effects.

5.0 CONCLUSION AND RECOMMENDATIONS

This study has shown the effects of brewery wastewater on water quality of Ikpoba River and its vulnerability to pollution owing to the fact that it serves as a receptacle for receiving brewery effluent with poor quality that failed to meet some of the minimum discharge requirements for wastewater discharge into rivers/streams (Table 2). The pH, COD, turbidity, Pb, Cu, Zn, BOD, COD, Ph, DO and TSS of Ikpoba river raw effluents were not within tolerable limits in comparison to standard effluent discharge requirements set by WHO and European discharge standards (see Table 2). The WQI calculated for the eight (8) different stations revealed severe pollution during the period of study. WQI calculated in March, 2014 ranged from -5200000 in SN1 to 2980000 in SN3; in May, 2014, WQI calculated was within the range of -5000000 in SN1 to -500000 in SN3. A similar result was obtained in July, 2014 as WQI values ranged from -3700000 in SN1 to 1200000 in SN3. Discharge locations and point source of waste had severe pollution while upstream locations were least polluted. Principal Component Analysis carried out on the selected parameter revealed copper as the only recurring parameter hence copper is the only component factor that triggers other parameters beyond tolerable limits. This indicates inefficient effluent treatment in the breweries hence there is heavy organic load from these waste on the river. In view of the above results and conclusion, an efficient water conservation and effluent management system should be designed by Guinness Nigeria plc to improve the water quality of Ikpoba River at discharge and downstream locations. This study therefore recommends the utilization of Activated carbon adsorption column in the treatment of brewery wastewater due to its efficiency in heavy metal removal from brewery effluent.

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