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Investigating the Nutrient Load from River Benue Water at the Reach of Makuredi-Nigeria

[1]Enokela O.S, [2]Utor S.O, [3]Awulu J.O.

[1]Department of Agricultural and Environmental Engineering, Joseph Sanwuan Tarka University Makurdi
enokladish@gmail.com
[2]LoS Water Engineering Nig Ltd, Suit DO5 J-Pius Plaza, 38 Jimmy Carter Street, Asokoro Abuja
3Department of Agricultural and Environmental Engineering, Joseph Sanwuan Tarka University Makurdi

Abstracts: *River Benue water at the reach of Makurdi was investigated for nutrient load using; multivariate statistics within a span of four (4) months from August to November, 2020 . A total of 36 raw water samples of the river were collected along and across the river at nine (9) sampling stations and analyzed using Atomic absorption spectrometer (AAS). Spatial variations of the nutrients* show *that the mean locational (station) concentration of TDS (mg/L) was highest Wurukum SB and the lowest in Abua NB. Phosphate and Nitrate were highest and lowest in Abua SB and Wurukum NB, and Wurukum MS and Abua SB respectively. Mean standard deviation were 312.2, 9.8, 1.55. 12.03, 0.74, 0.04, and 8.70 for. Turbidity, TDS, K, Na, Mg,* NO_3*,* NH_3^+*, and* PO_4^- *respectively. Turbidity was found to be the greatest influence towards the poor water quality of the river. Principal component analysis revealed four principal components (PCs) with Eigen values greater than 1, PC1 and PC2 accounted for about 70% of the total variance observed, an indication that the parameters in PC1 and PC2 were responsible for the high pollution levels of the river. Hierarchical cluster analysis (HCA) further proved that, nutrients were of similar origin (agricultural activities), contributing majorly to the overall poor water quality status of the river.*

Keywords---Water: River Benue: Nutrient load: Quality index: Multivariate statistic

1. INTRODUCTION

Pollution of fresh water bodies, especially the rivers is no longer within safe limits for human consumption as well as aquatic fauna which can be measured by nutrient load from the water. [1] reported about 70% of India's surface water resources and a growing percentage of its groundwater reserves been contaminated by biological, toxic, organic and inorganic pollutants due to mismanaged disposal of industrial effluents, domestic wastes and agricultural pollutants. Presence of nutrients from agricultural runoff in large volume of water could reduce the biological oxygen demand to such a great level that the entire oxygen may be removed. The impact of agriculture on surface and groundwater is determined as negative and this would cause the death of all aerobic species including fishes [2]. These may be derived from inputs of suspended solids to which toxic substances are absorbed; such as soil particles in surface water run-off from fields treated with pesticides. Pesticides are useful tools in agriculture but their contribution to the gradual degradation of the aquatic ecosystem cannot be ignored [3].

Agricultural run-off of pesticides, herbicides, plants and animals wastes is a major contributing source of organic pollution to water bodies in Nigeria. The work of [4] had linked the periodic eutrophication of Oyun Reservoir in Offa, Kwara State to run-off of phosphate fertilizers from nearby farms in addition to cow dungs washing from the watershed into the Reservoir. Water pollution through surface run-off has been reported in literatures with subsequent effects on nutrient enrichment, water quality impairment, marine lives spawning ground destruction and fish killed [5].

Most contaminants affecting water quality comprise simple inorganic ions, more complex organic molecules, nitrate, phosphorus, pesticide, soil sediment, salt, particulates and pathogen pollution. These can derive from various sources, including soils and decomposing vegetation, but also from animal manure [6]; [7]; [8]. Agricultural activities that can cause pollution include poor animal husbandry practices; overgrazed grasslands; over and excessive use including untimely application of pesticides, ploughing over irrigated fields and application of fertilizers.

There is considerable agreement in recent studies that amounts of nitrogen and phosphorus in surface waters are significantly influenced by anthropogenic inputs associated with land cover, land use and point sources [9]. Pollutants that result from farming and cattle breeding are comprised of nutrients, sediments, pathogens, pesticides, metals and salts.

2. THE STUDY AREA

River Benue is one of the major rivers in Nigeria. It starts from Cameroonian mountains and flow westwards through Makurdi to meet the River Niger at Lokoja in Kogi State. Its tributaries include but not limited to Rivers Donga, Katsina-Ala, Bantaji and Taraba. Along the Makurdi New Bridge, the river is 1.194Km wide with average depth and cross sectional area of 7.82m and 4608.42m^2 respectively [10]. The valley of the river which is covered with meta sediments consists of land area below 300m above sea level. The flood plain, which is characterized by extensive swamps, is good for dry season irrigated farming. River Benue provides natural water and sand in commercial quantities to the environs. Benue Roof Tiles Company is a beneficiary of the natural resource.

Water from River Benue is used for domestic, industrial and agricultural purposes to supplement the existing surface water source in areas not covered by the current distribution network [11]. Considering the fact that, Makurdi is growing and River Benue is the major source of water supply for the inhabitants, incidences of water related diseases in this area has necessitated the decision to study its raw water quality parameters especially as it affects man.

At the reach of Makurdi, the river is subjected to various sources of pollution. Industrial wastes from Benue Brewery Limited (BBL) and Nigeria Bottling Company (NBC) all are channeled into river. Also, wastes from markets and abattoir are washed into the river. Other sources of pollution of the river are faeces from humans defecating directly in the river, animal and human wastes washed from land to the river as well as fertilizers and other chemicals applied to the crops that are usually grown at the river banks [12].

3. MATERIALS AND METHOD

3.1 Sampling Protocol

Three water samples were collected along the North-Middle-South transect of the River at three sampling locations making a total of 36 samples by grab method according to [13]. The sampling points and their respective coordinates are as shown in Table 1. Samples were collected in 2 litres capacity plastic bottles during the period August – November, 2020. The sample bottles were rinsed with nitric acid, followed by distilled water and then with the River water before sample collection. The sample bottles with water samples were properly labeled; parameters such as temperature, pH, turbidity, total dissolved solids and conductivity were determined in-situ, immediately after the sample collection. The samples were then stored in an ice cooler and transported to the National Research Institute for Chemical Technology (NARICT), Zaria for determination of other water quality parameters. A total of 7 nutrient parameters namely, turbidity, total dissolved solids, sodium, potassium, nitrate, phosphate and ammonium were monitored throughout the study. All measurements were done in duplicates and mean values reported to guarantee the reproducibility and reliability of the data as well as take care of any experimentally induced errors.

3.2 Laboratory analysis

The presences of nutrients (TDS, sodium, magnesium, potassium, nitrate, ammonium and phosphate) were determined through the use of an Atomic Adsorption Spectrophotometer (PG 990 AAS) in accordance with the method described by [14].

Each sample (150ml) was transferred into a beaker and 5ml of concentrated HNO_3 added. The beaker with the content were placed on a hot plate and evaporated down to about 20ml. The beaker was then been cooled and another 5ml of concentrated HNO_3 added. Each beaker was then covered with a watch glass and returned to the hot plate for more heating with the addition of few drops of HNO_3 until the solution appeared light colored and clear (sample digestion). The walls of the beaker and the watch glass were washed down with distilled water and the sample filtered to remove insoluble materials that could clog the atomizer. The volumes of the samples were then made up to the mark (150ml) with distilled water [15]. A blank sample was similarly treated so as to give room for blank correction. This was done by transferring 150ml of distilled water into a beaker and digested as described above. Calibration standards were prepared from the stock solutions by dilution and matrix matched with the acid concentration of the digested samples. The digested samples were then analyzed using the corresponding ASS lamps for each nutrient load.

3.3 Experimental Design and Data Analysis

Data of the current study was analyzed using descriptive statistics for each nutrient load and location considered in the study. Furthermore, water quality index, multivariate statistics and risk analysis were used to assess the pollution levels of river Benue water at Makurdi especially as it concerns nutrient loads in accordance with the methods described by [16]. ANOVA was used to establish significant differences in the parameters at the different locations and times considered in the study.

3.4 Multivariate statistics

Correlation, Principal Component (PC) and Cluster analyses were used to further assess the nutrient load of River Benue water at Makurdi and the interrelationship of the nutrient parameters. This was aimed at revealing the sources or factors contributing to nutrient load of the river water at the studied locations and times.

The degree of linear association between the nutrient parameters was measured by the simple correlation coefficient (r). Correlation analysis measures the closeness of the relationship between chosen variables; if the correlation coefficient is nearer to +1 or –1, the linear relationship between the two variables is perfect [17]. In this study, the Pearson's pair-wise correlation (r) was used to determine the inter-parameter relationship, where the contributions of each nutrient as well as their possible sources can be exposed with the confidence interval for this analysis kept at 95% or 90% where applicable using the Statistical Package for Social Sciences software (SPSS Version 21).

Furthermore, Principal Component Analysis (PCA) was employed to identify the parameters significantly contributing to the nutrient load of the river by dimension reduction of selected parameters. To achieve this, the Standardized Principal Component Analysis (SPCA) using Varimax rotation (orthogonal rotation) was employed to normalize the parameters due to variability. Moreover, the measured parameter were also used to obtain the influence plot, scree plot, score plot, and loading plot, again using Statistical Package for Social Sciences software (SPSS Version 21).

After identifying the major hidden nutrient load sources in the river, the next step was to examine the similarity among considered stations and months for possible zonings according to the level of existing pollution. For this purpose, Cluster Analysis (CA) was used to decide which of the sampling points (stations) or months are most similar to each other, considering all of the nutrient load simultaneously. Cluster analysis employs the familiar concept of distance, considering two points, i and j, with coordinates ($X_1i; X_2i$) and ($X_1j; X_2j$), respectively; the Euclidian distance between the two points is hypotenuse of the triangle ABC expressed as:

$$D_{(I,\, j)} = (A^2+B^2)^{1/2} = \{(X_{1i}-X_{1j})^2 + \{(X_{2i}-X_{2j})^2\}^{1/2}. \quad (1)$$

4. RESULTS

The results for the mean monthly and mean locational (station) turbidity and concentration of nutrient parameters are as shown in Figures 1 and Figure 2 respectively in the water samples. Table 1 shows range, overall means and SD of the studied nutrient parameters for all stations and sampling periods considered in comparison with the WHO standard limits for drinking water.

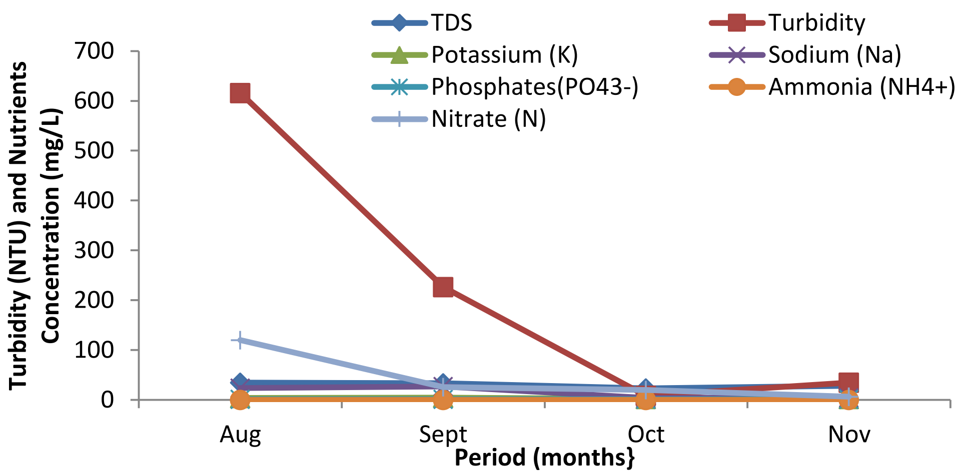

Figure 1: Mean Variations of monthly Turbidity and Concentration of Nutrients in River Benue Water

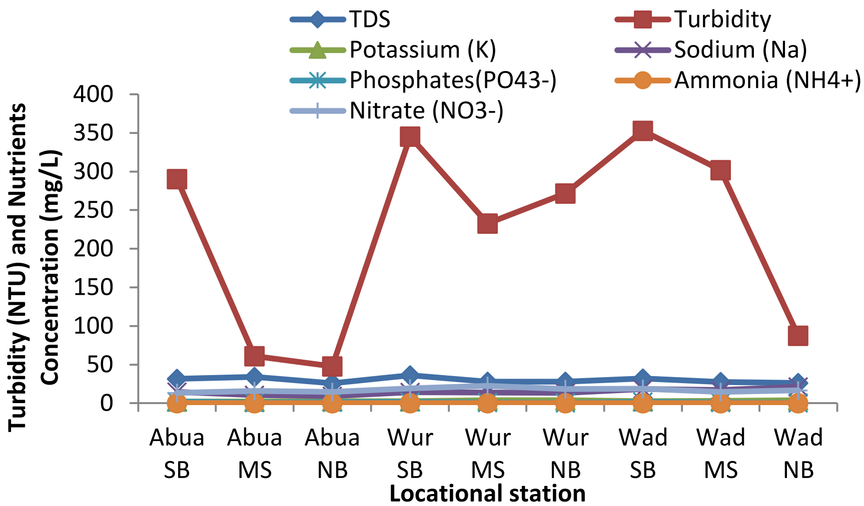

Figure 2: Mean Locational Turbidity and Nutrients Concentrations of River Benue Water
Note: SB-south bank; MS-mid stream and NB- north bank

Table 1: Overall Variations in Nutrient load of River Benue Water

S/No	Parameter	Minimum	Maximum	Mean ±S.D	WHO Limit	%Violation/ Compliance
1	TDS	18.41	53.80	29.90 ± 9.83	700	0/100
2	Turbidity	5.30	996.00	221.31 ±312.22	5	100/0
3	Potassium	1.30	6.86	2.95 ±1.55	10	0/100
4	Sodium	2.80	38.80	14.74 ±12.03	200	0/100
5	Phosphate	0.32	3.88	1.24 ±0.74	0.70	77.8/22.2
6	Ammonium	0.01	0.18	0.07 ±0.04	0.5	0/100
7	Nitrate	5.80	34.24	17.13 ±8.70	50	0/100

Note: 'N' = 36 and all parameters are in mg/L, except turbidity (NTU).

From Figure 1 it can be seen that the mean monthly variation of turbidity (NTU) were found to be in the range of 8.29 - 616.00 with the highest and lowest values observed in the months of August and October respectively. Also the mean monthly concentration of TDS (mg/L) in the water samples ranged from 23.03 - 34.88, with the highest values recorded in October and the lowest in the month of August. Phosphate and Nitrate were found to be in the ranges of 0.99 - 1.42 mg/L and 6.44 - 25.43 mg/L respectively with the highest and lowest values observed in the months of September and November respectively in each case. The concentrations of ammonium (mg/L) in the water samples were observed to be very low and ranged from 0.05 in August to 0.08 in the month of September.

The mean locational (Abua NB, Abua MB, Abua SB, Wurkum NB, Wurkum MB, Wurkum SB, Wadata NB Wadata MB and Wadata SB) concentration of TDS (mg/L) in the water samples ranged from 25.86 - 36.06, with the highest values recorded in station 4 (Wurukum SB) and the lowest in station 3 (Abua NB). Phosphate and Nitrate were found to be in the ranges of 0.60 - 2.01 mg/L and 13.24 - 22.46 mg/L respectively with the highest and lowest values observed in stations 1 (Abua SB) and 6 (Wurukum NB), and stations 5 (Wurukum MS) and 1 (Abua SB) respectively. Similar to the monthly variations, the concentrations of ammonium (mg/L) in the water samples were observed to be very low and ranged from 0.035 in stations 5 and 6 to 0.14 in station 2. For the nutrients contents i.e phosphate, ammonium and nitrate, the concentrations in the river water ranged from 0.32 - 3.88, 0.01 - 0.18 and 5.80 - 34.24. Mean standard deviation were 312.2, 9.8, 1.55. 12.03, 0.74, 0.04, and 8.70 for. Turbidity,TDS, K, Na, Mg, NO_3, NH_3^+, and PO_4^- respectively.

4.1 Nutrient Load Index (NLI)

The (NLI) computations on the water samples was based on all nutrient parameters (mg/L) for each sampling station and period (months) including turbidity because these parameters are of less importance for human health concerns and moreover, the turbidity values recorded in this study were found to be extremely high for the months of August and September and thus contributed exceptionally to the NLI. This contribution was assumed to be hypothetical as turbidity of the water could be greatly reduced by simple cloth or sand filtration and thus was not taken to be of great risk to humans who consumed the water.

Figure 3 show the NLI of the river for each period (August – November) and station (1-9) of sampling, while Figure 4 is the plot of the NLI for all sampling location/station using the means values of parameters for all sampling stations and periods. This was highest in August because of early cropping season in June and July with high use of fertilizers and agrochemicals which are subsequently discharged into the river body as agricultural runoff. It also connote period of low river discharge hence more concentration of nutrients in water solution. The trend deceases as volume of discharge increases but a striking rise in November corresponding to lower steam discharge. Table 3 shows the WQI classification used for classifying river Benue water at the various sampling stations and period [16]. From Figures 3 it was observed that the NLI for the month of August ranged from 149.8 – 529.1 with the highest and lowest values recorded for stations 4 (Wurukum SB) and 3 (Abua NB) respectively. The water obtained in the month of August for most sampling stations exceeded the threshold value of '300' and could be classified into class V (Water unsuitable for drinking) for such sampling stations with the exception of stations 4, 5, 6 and 1, 2 whose WQI fell into classes III (Poor water) and IV (very poor water) respectively.

However, a different trend was observed for the month of September as NLI ranged from 73.61 - 149.89, with the highest and lowest values observed for stations 3 and 4 respectively. The water obtained from most of the sampling stations in the month of September could be grouped into class II (good water) of the WQI classification with exception of stations 5 and 6 whose WQI fell into class III (poor water).

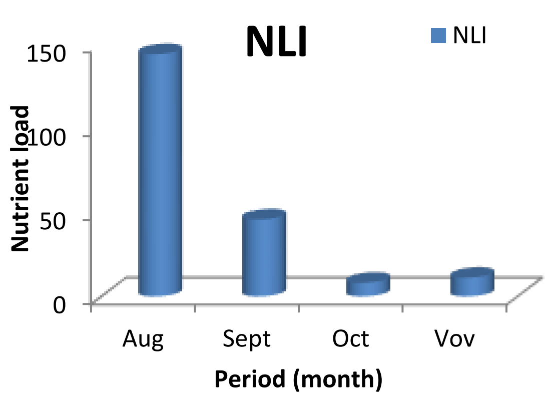

Figure 3: NLI of the river for each period (August – November)

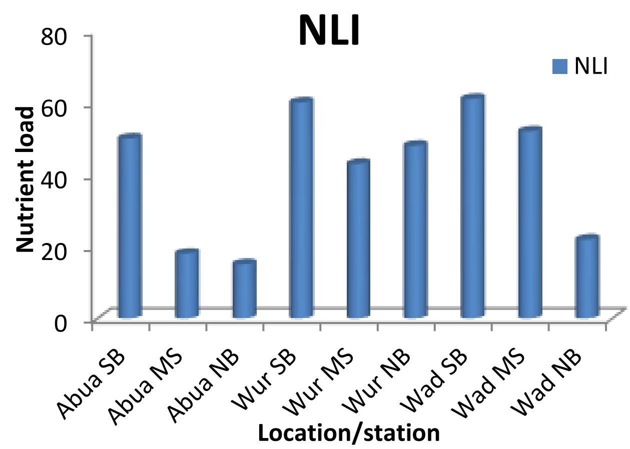

Figure 4: NLI of the river for each location/station

Sampling for the month of October revealed a striking rise in the NLI for Abua SB (7758.8) which was 25.86 times higher than the threshold value of 300 for water that is unsuitable for drinking. Generally, NLI for the month of October ranged from 74.35 - 7758.8 with the

Table 3: Water Quality Classifications use in the Study

WQI	Class	Type of Water
< 50	I	Excellent Water
50.1 – 100	II	Good Water
100.1 – 200	III	Poor Water
200.1 – 300	IV	Very Poor Water
>300	V	Water unsuitable for drinking

Source: Al-Omran *et al.*, (2015)

4.2 Statistical Analysis

The data obtained from the correlation analysis served as a proportional measure to represent the association of one variable with the other. This study examined the interrelationships among the water nutrient load parameters studied. In accordance with [18]; [19], if the correlation coefficient (r) is less than 0.3, the relationship is regarded as a weak correlation, if it ranges from 0.3 to 0.7, the relationship is considered as moderate, and when the value of r is greater than 0.7 it is considered strong. Results of correlations of the studied water quality parameters are shown in Table 4. From Table 4, it was observed that TDS exhibited a moderately positive relationship with turbidity (r = 0.462) and Na (r =

0.327). Turbidity was found to have a moderate and positive relationship with K (r = 0.414), Na (r = 0.618) and Mg (r = 0.577). Potassium exhibited a strong positive correlation with Na (r = 0.752) and Mg (r = 0.843) and nitrate (r = 0.486), while it showed a moderately negative correlation with Ni (r = -0.336) and ammonium (r = -0.333). Similarly, sodium had a strong positive correlation with Mg (r = 0.941), and moderately negative correlation nitrate (r = 0.453).

5. DISCUSION

Table 4: Correlation Matrix of Nutrient Load Parameters

	TDS	Turbidity	Potassium	Sodium	Phosphate	Ammonium	Nitrate
TDS	1						
Turbidity	0.462 (0.005)**	1					
Potassium	0.109 (0.528)	0.414 (0.012)*	1				
Sodium	0.327 (0.051)	0.618 (0.000)**	0.752 (0.000)**	1			
Phosphate	-0.026 (0.879)	0.032 (0.853)	-0.073 (0.670)	0.115 (0.504)	1		
Ammonium	0.062 (0.718)	-0.187 (0.276)	-0.333 (0.048)*	-0.104 (0.546)	0.264 (0.120)	1	
Nitrate	0.167 (0.331)	0.245 (0.150)	0.486 (0.003)**	0.453 (0.006)**	0.108 (0.532)	-0.091 (0.597)	1

Turbidity: Turbidity in the water may be due to organic and or inorganic constituents. It is often determined and used as surrogate measure of total suspended solids [20]. The current study recorded the mean turbidity of 500.65NTU. This result exceeds the recommended standard value for turbidity of 5.00NTU [21]; [22], thus disagrees with the findings of an earlier study in River Benue that reported a mean turbidity value of 4.88NTU [23].

The extremity of turbidity result in the present investigation may be due to surface run off and incessant waste disposal into the River during the study period. [24] reported higher mean value of 550.00 NTU turbidity in Challawa River, Kano State Nigeria during his study which slightly agrees with the findings of the current study.

TDS: The total dissolved solids in water consist of inorganic salts and dissolved materials. High values of TDS may lead to change in taste of water and deteriorate plumbing fittings and appliances. The present investigation recorded a mean TDS value of 36.12mg/L which falls within the [21] standard value of 1000.00mg/L and 500.00mg/L of the national standard for drinking water quality [22]. The low concentration level of TDS recorded may be due to the self-purification capacity of lotic water body with distance. [25] reported lower values of 18.50mg/L in a drainage channel in south western Nigeria.

Phosphate: Phosphorus is present in the form of phosphate in natural waters and generally occurs in low concentration. Phosphorus is a nutrient for plant growth and a fundamental element in the metabolic reaction of plants and animals [26]. Phosphorus also controls algal growth and primary productively in surface waters, however, excess amounts of phosphorus can result to eutrophication leading to excessive algal growth [26]. In most natural waters, phosphorus usually ranges from 0.005 - 0.020mg/L. In the present study, mean phosphorus concentration of 2.1mg/L was obtained. This result is well below the result of earlier study in River Benue that reported mean phosphate concentration of 5.34mg/L [23]. Similar higher trends of phosphorus in the range of 2.60 - 5.56 mg/L were reported in Abesan River, Lagos [27]; [28] reported an infinitesimal phosphate in River Benue in range of 0.07 - 0.17mg/L. Nevertheless the result of this study agrees with that of Ogunpa River at Bodija, Ibadan Oyo State [29]. Similarly, [30] reported a mean phosphorus value of 0.05 in a Creek in Niger Delta, which disagrees with the result of this study. [25] also reported low values of less than 1.00mg/L of phosphorus during their study period. Phosphate concentration obtained in this investigation is probably attributed to surface water runoff that washes fertilizer residues from farm lands into the river.

Nitrate: The presence of nitrate in a lotic system mostly depends on the activity of nitrifying bacteria, stream currents and the characteristics of the catchments area, domestics as well as agricultural sources. In this study, the mean concentration of nitrate was 20.02mg/L. This result is though lower but within the recommended standard of 50.00mg/L permissible limits of nitrate for safe drinking water quality

[21]; [31]. Similar trends of nitrate were reported in surface waters by [27]; [29]. The low mean nitrate value in this study may be due to the activities of nitrifying bacteria in the River. [32] reported even lower nitrate concentration in the surface waters.

***Ammonium*:** Ammonia in water is an indicator of possible bacteria, sewage and animal waste pollution according to WHO guidelines for drinking water quality (fourth edition), 2011 and Nigerian standard for drinking water quality, 2007. Certain bacteria oxidize ammonia rapidly to nitrite and nitrate in a process that involves DO. Ammonia been a source of nitrogen is also a nutrient for algae and other forms of plants life, thereby, overloading the natural water and causing pollution. In this research work, the highest value for ammonia was 0.18gm/L and the lowest value was 0.01mg/L with a mean value of 0.1mg/L which is higher than the permissible limit for drinking water, and could be attributed to anthropogenic activities that takes place in and around the river.

6 CONCLUSION

The assessment of river Benue water at Makurdi, North central Nigeria considering spatial (axial and longitudinal) variations of nutrient load index, source apportionment /pollutants interrelationships using multivariate statistics, and the human health risk was undertaken in the current study.

Correlation analysis revealed strong, moderate and weak positive/negative relationships among pollutants. Strong positive relationships were observed for TDS and EC, K, Na and Mg. Principal Component analysis revealed four principal components (PCs) with Eigen values greater than 1. Majorly, PC1 and PC2 accounted for about 70% of the total variance observed. PC1 was positively and strongly loaded with NH_4^+, PO_4^-, TDS. PC2 was found to be strongly and positively loaded in phosphate turbidity and TDS, while it was weakly and positively loaded in nitrate and ammonium. This was an indication that the parameters in PC1 and PC2 were responsible for the high pollution levels of the river. These pollutants were inferred to originate mainly from agricultural practices around the river banks as well as from ion exchange and rock dissolution processes.

HCA also classified the sampling points in terms of similarity in pollution levels and showed that stations 2, 3 and 9 which were characterized by heavy agricultural practices and moderate commercial activities had similar pollution status and were the most polluted stations among the nine considered.

It was concluded that the river Benue water at Makurdi is currently heavily polluted as a results of unregulated agricultural and commercial activities on the river banks, which pose risk to the inhabitants that uses the water for the purposes of drinking. Furthermore, the use of the water for bathing and recreation at some stations could also be injurious to human health.

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