

## SEASONAL VARIATION IN HYDRO CHEMISTRY OF RIVER BENUE AT MAKURDI, BENUE STATE NIGERIA.

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**ABSTRACT:** *The hydrochemistry of River Benue at Makurdi was studied for two years (July 2011-June 2013). Water samples were collected monthly from five different Stations on the shoreline of River Benue at Makurdi. The hydrochemistry of the water samples were examined using standard methods. The results of the physico-chemical parameters indicate the river water samples with the following characteristics: conductivity ranged from  $139\pm 215.05\mu\text{S}/\text{cm}$  -  $63.95\pm 30.94\mu\text{S}/\text{cm}$ , pH varied from  $6.33\pm 0.59$ - $6.95\pm 0.86$ , TDS varied from  $28.29\pm 11.69\text{mg}/\text{L}$ -  $69.14\pm 106.65\text{mg}/\text{L}$ , TSS varied from  $41.00\pm 25.42\text{mg}/\text{L}$ -  $87.56\pm 57.39\text{mg}/\text{L}$ , colour ranged from  $192.60\pm 143.79\text{TCU}$ - $393.01\pm 175.73\text{TCU}$ , turbidity ranged from  $44.53\pm 44.28\text{NTU}$  -  $91.38\pm 56.54\text{NTU}$ , surface water temperature ranged from  $28.09\pm 1.97^{\circ}\text{C}$  -  $28.99\pm 1.63^{\circ}\text{C}$ , bicarbonate ranged from  $121.98\pm 59.13\text{mg}/\text{L}$  -  $185.61\pm 57.20\text{mg}/\text{L}$ , chloride ranged from  $117.44\pm 59.46\text{mg}/\text{L}$  -  $173.07\pm 71.27\text{mg}/\text{L}$ , nitrate ranged from  $2.23\pm 3.14\text{mg}/\text{L}$  -  $3.76\pm 5.22\text{mg}/\text{L}$ , sulphate ranged from  $10.41\pm 9.84\text{mg}/\text{L}$ -  $17.24\pm 15.21\text{mg}/\text{L}$ , phosphate ranged from  $0.92\pm 1.11\text{mg}/\text{L}$ -  $1.47\pm 2.07\text{mg}/\text{L}$  and copper ranged from  $0.11\pm 0.09\text{mg}/\text{L}$ -  $0.31\pm 0.34\text{mg}/\text{L}$ . The mean values were generally within the WHO and the Nigerian Standard for Drinking Water Quality accepted maximum limit except for colour and turbidity. The result of ANOVA for all the parameters was significant during the seasons ( $P < 0.05$ ), except for TDS, TSS and temperature ( $P > 0.05$ ). Across the Stations temperature, bicarbonate, nitrate, sulphate, phosphate and copper were not significant (ANOVA,  $P > 0.05$ ). Generally the wet seasons had more values as compared to dry months. It is recommended that the discharged of effluents and other waste into the River Benue should be controlled and enforced.*

**KEYWORDS:** Hydrochemistry, Seasonal variation, River Benue, Makurdi

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## INTRODUCTION

The hydro chemistry parameters of lakes, ponds and rivers have considerable effect on the aquatic life. These Parameters determine the productivity of a water body. Thus, a change in the hydro chemistry aspect of a water body brings about a corresponding change in the relative composition and abundance of the organisms in that water (Adeyemi *et al.*, 2009). Meteorological events and pollution are a few of the external factors which affect physico-chemical parameters such as temperature, pH and DO, of the water (Hacioglu and Dulger, 2009). These parameters have major influence on biochemical reactions that occur within the water. Sudden changes of these parameters may be indicative of the changing conditions of the water (Hacioglu and Dulger, 2009). Internal factors on the other hand include events which occur between and within the biota population in the water body (Bezuidenhout *et al.*; 2002).

The water temperature is one of the most important physical characteristic of ecosystem. It affects a number of water quality parameters that are concern for domestic, environmental, industrial and agricultural applications (Parashor *et al.*, 2007). The chemical and biological reaction rates increases with increase in water temperature (Parashor, *et al.*, 2007. UNEP, 2006). The pH of an aquatic ecosystem is important because it is closely linked to biological productivity. Although the tolerance of individual species varies, pH values between 6.5 and 8.5 usually indicate good water quality and this range is typical of most major drainage basins of the world (UNEP, 2006). Similar studies carried out by Abowei ( 2010) indicates that pH values higher than 7 but lower than 8.5 is ideal for biological productivity, while pH lower than 4 is detrimental to aquatic life. The greater the amount of suspended solids in the water, the murkier it appears and the higher the measured turbidity (UNEP, 2006). Conductivity provides good indication of the changes in water composition particularly its mineral concentration (Ezekiel *et al.*, 2011). Variations of dissolved solids in water could affect the relative quantities of the various components. Phosphate ions are not desirable in surface water, because they act as the most important growth limiting factor in eutrophication and result in a variety of adverse ecological effects (Fatoki, *et al.*, 2001). Untreated storm water runoff from urban areas can contain levels of some parameters (e.g. total dissolved solids) that exceed those found in untreated waste water (Walsh *et al.*, 2002). These pollutants entering water bodies as a result of urbanization can be harmful to aquatic animals (EdoKpayi *et al*; 2010). The many chemical compounds dissolved in water may be of natural or industrial origin and may be beneficial or harmful depending on their composition and concentrations (Henry and Heinke, 2005). Colour from textile, dyeing and foam from pulp and paper mill wastes are not just aesthetically objectionable, they also limit light penetration and can reduce dissolved oxygen levels, both of which upset the natural ecological balance in the water (Henry and Heinke, 2005).

## MATERIALS AND METHOD

### Study Area

The River Benue with its source in the Cameroonian mountains flows westwards into Nigeria. It is the second largest river in Nigeria and measures approximately 310,000 Ha. It is about 1.488Km in length with alluvia fertile flood plains on either banks (Welcomme, 1986). The Benue River flows through Makurdi and confluence with River Niger at Lokoja the capital of Kogi state, Nigeria. Makurdi the capital city of Benue state is located on Latitude 7<sup>o</sup>41' N and Longitude 8<sup>o</sup> 28' E. The size of the River Benue within Makurdi and major settlement runs through is approximately 671 meters (Udo, 1981). The rainfall seasons at Makurdi produces a river regime of peak flows from August to early October and low flow from December to April. The rainy season which last for seven months (April to October) has a mean annual rainfall ranging from 1200-2000mm (Nyagba, 1995). High temperature values averaging 28-33<sup>o</sup>C are recorded in Makurdi throughout the year, most notable from March to April. Harmantan winds are accompanied with cooling effects mostly during the nights of December and January (Nyagba, 1995). All the same the periodic dust plumes associated with this time of the year may encourage surface water pollution (Nyagba, 1995). Five stations were selected along the river course at Makurdi , Benue state as indicated in Fig 1 for this study are as follows:

Site I(N07<sup>o</sup> 43.663' E008<sup>o</sup> 35.427'): it is located behind Coca cola plc plant along Gboko road and it is approximate 1.5 kilometers away from Site II

Site II (N07<sup>0</sup> 43.615' E008<sup>0</sup> 35.300'): it is located directly behind Benue Brewery Plc along at Kilometer 5 along Gboko road. This site is impacted by the brewery effluents generated from the factory into the river.

Site III (N07<sup>0</sup> 43.649' E008<sup>0</sup> 35.302'): this site is located behind Mikap Nigeria Ltd, a rice processing factory along Gboko road. It is approximately 1 kilometer away from Site II and 2.5 kilometers away from site I. This site receive effluents from the rice mill into the river

Site IV (N07<sup>0</sup> 44.076' E008<sup>0</sup> 32.840'): this site is located behind Wurukum abattoir close the new bridge across the river. Abattoir waste is washed directly into this site. Farming and sand dredging also take place at this site on routine bases.

Site V (N07<sup>0</sup> 44.789' E008<sup>0</sup> 30.624'): This site is located behind Wadata market along the river water course at Makirdi. Wastes from the heap refuse dumpsite behind the market are leached directly into the river.

### **Water Sample Collection and Analysis**

Water samples for physico-chemical analysis were collected at five different points from each of the five sampling Stations. Fortnightly routine sampling was conducted between 8:00am and 12:00 noon on each sampling day. The water samples for biochemical oxygen demand analysis were collected in dark bottles of 1,500 mL capacity at the depth of 20cm, while 1,500mL (1.5L) containers were used for collection of water samples for the other physico-chemical parameters. Usually sampling bottles and containers were rinsed three times with River water at each sampling site before sample collection. The water sampler was rinsed for about six times at each sampling site before the collection of the samples. Each sample container was treated according to the analysis to be carried out on it on the field before they were transported to the laboratory. Surface water temperature, TDS, Conductivity, and pH were determined in situ on the field, while copper, nitrate, chloride, bicarbonate, sulphate, phosphate, TSS, turbidity and colour, were examined in the laboratory using standard methods (APHA,1999).

### **Data Analysis**

Microsoft excel 2007 was used for graphical illustrations. Means were determined using SPSS version 20. ANOVA was determined to test the significant difference among means of water quality parameters across stations and between seasons.

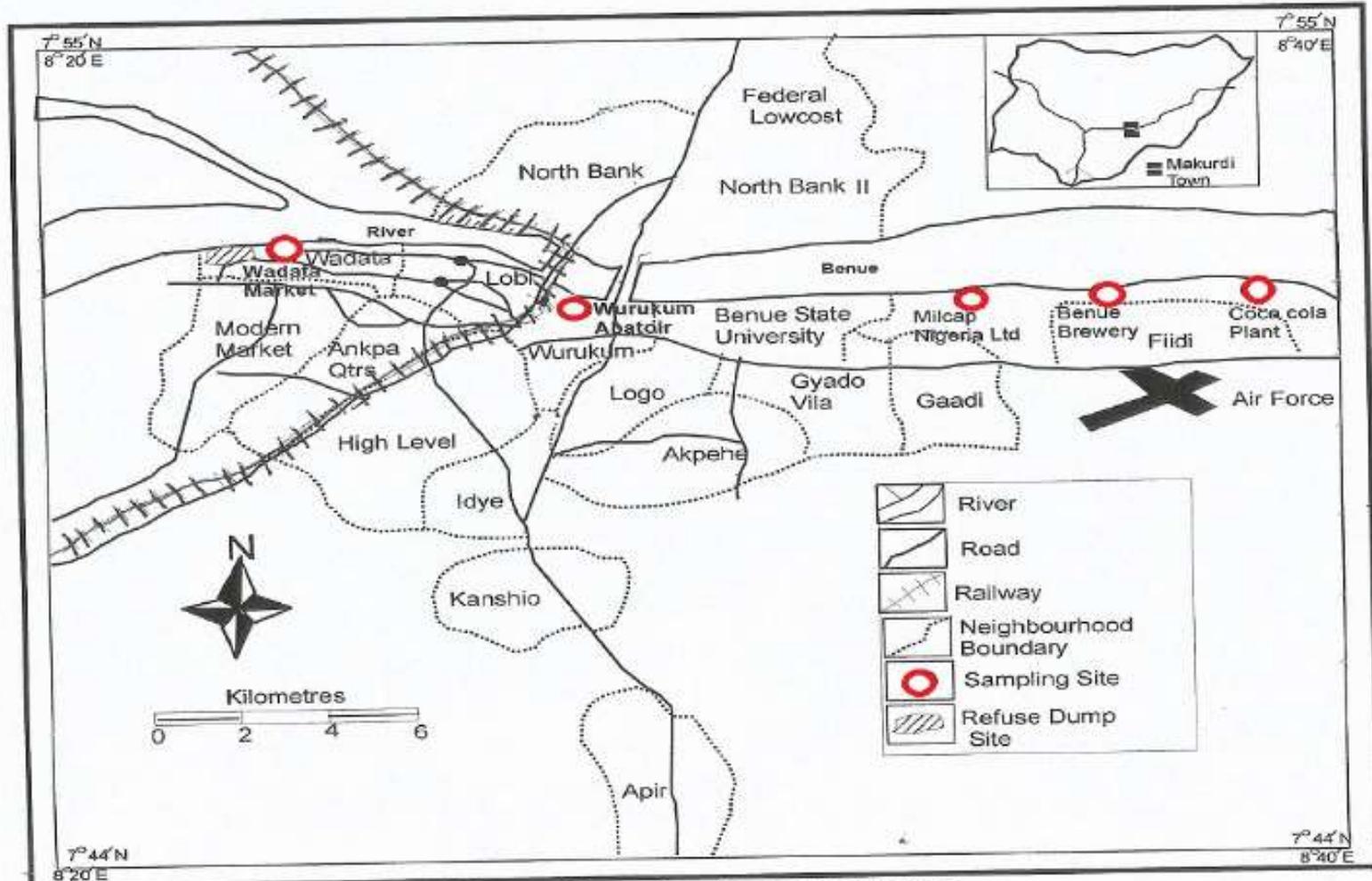


Figure 1: Map of Makurdi Town Showing Sampling Sites

Source: Ministry of Lands and Survey Makurdi

## RESULTS

The variation in the physico-chemical parameters of within sampling stations and across the seasons are presented in Table 1 and 2 respectively. The results of the physico-chemical parameters at the station in Table 1 indicates that conductivity ranged from  $139 \pm 215.05 \mu\text{S}/\text{cm}$  -  $63.95 \pm 30.94 \mu\text{S}/\text{cm}$ , pH varied from  $6.33 \pm 0.59$  -  $6.95 \pm 0.86$ , TDS varied from  $28.29 \pm 11.69 \text{mg}/\text{L}$  -  $69.14 \pm 106.65 \text{mg}/\text{L}$ , TSS varied from  $41.00 \pm 25.42 \text{mg}/\text{L}$  -  $87.56 \pm 57.39 \text{mg}/\text{L}$ , colour ranged from  $192.60 \pm 143.79 \text{TCU}$  -  $393.01 \pm 175.73 \text{TCU}$ , turbidity ranged from  $44.53 \pm 44.28 \text{NTU}$  -  $91.38 \pm 56.54 \text{NTU}$ , surface water temperature ranged from  $28.09 \pm 1.97^\circ\text{C}$  -  $28.99 \pm 1.63^\circ\text{C}$ , bicarbonate ranged from  $121.98 \pm 59.13 \text{mg}/\text{L}$  -  $185.61 \pm 57.20 \text{mg}/\text{L}$ , chloride ranged from  $117.44 \pm 59.46 \text{mg}/\text{L}$  -  $173.07 \pm 71.27 \text{mg}/\text{L}$ , nitrate ranged from  $2.23 \pm 3.14 \text{mg}/\text{L}$  -  $3.76 \pm 5.22 \text{mg}/\text{L}$ , sulphate ranged from  $10.41 \pm 9.84 \text{mg}/\text{L}$  -  $17.24 \pm 15.21 \text{mg}/\text{L}$ , phosphate ranged from  $0.92 \pm 1.11 \text{mg}/\text{L}$  -  $1.47 \pm 2.07 \text{mg}/\text{L}$  and copper ranged from  $0.11 \pm 0.09 \text{mg}/\text{L}$  -  $0.31 \pm 0.34 \text{mg}/\text{L}$ . The result presented in Table 2 depicts that except for

bicarbonate and phosphate all the other parameters recorded their highest mean concentration during the wet seasons as compared to the dry season during the period of this study. All the same there were instances in which the concentration of the parameters was alternating between the seasons. Surface water temperature showed little variations across the seasons during the course of the study.

**Table 1: Mean Concentration of Physico-chemical Parameters of River Benue at Makurdi**

Parameter	Unit	Sample Station Codes				
		I	II	III	IV	V
Conductivity	µS/cm	64.69±36.97	124.79±125.52	139.59±215.05	63.95±30.94	70.97±48.57
pH		6.95±0.86	6.90±0.74	6.49±0.87	6.46±0.84	6.33±0.59
TDS	mg/L	35.05±18.18	67.15±68.79	69.14±106.56	28.29±11.69	34.89±27.97
TSS	mg/L	41.00±25.42	87.56±57.39	87.09±91.17	52.17±51.58	44.25±49.75
Colour	TCU	244.54±128.53	393.01±175.73	344.28±157.89	208.07±113.63	192.60±143.79
Turbidity	NTU	46.89±26.66	91.38±56.54	83.47±65.83	49.12±47.22	44.53±44.28
Temperature	°C	28.09±1.97	28.69±1.89	28.96±1.83	28.96±2.11	28.99±1.63
Bicarbonate	mg/L	122.52±57.20	185.61±126.59	182.69±178.63	121.98±59.13	126.66±69.85
Chloride	mg/L	145.19±109.98	173.07±71.27	169.72±82.86	117.44±59.46	138.56±83.32
Nitrate	mg/L	2.79±4.38	3.66±3.08	3.67±5.22	3.76±5.22	2.23±3.14
Sulphate	mg/L	10.95±15.84	16.40±18.98	17.24±15.21	12.55±11.84	10.41±9.84
Phosphate	mg/L	1.21±1.94	1.20±0.81	1.47±2.07	1.25±2.49	0.92±1.11
Copper	mg/L	0.16±0.27	0.31±0.34	0.24±0.28	0.12±0.27	0.11±0.09

**Table2: Seasonal Variation in Physico-chemical Parameters in River Benue at Makurdi**

Parameter	Unit	Seasonal Variation				
		Wet season (S <sub>1</sub> )	Dry season (S <sub>2</sub> )	Wet season (S <sub>3</sub> )	Dry season (S <sub>4</sub> )	Wet season (S <sub>5</sub> )
Conductivity	µS/cm	101.39±31.31	58.24±54.82	58.65±40.44	135.13±216.49	148.07±127.35
pH		7.51±0.97	6.35±0.41	6.22±0.37	6.81±0.83	6.56±0.89
TDS	mg/L	36.29±14.78	32.04±29.95	37.46±32.91	69.77±109.07	69.78±63.09
TSS	mg/L	36.85±41.24	61.20±59.94	67.07±53.92	67.65±80.37	78.95±65.52
Colour	TCU	140.10±57.32	247.44±171.16	324.88±166.05	304.81±150.94	346.73±160.14
Turbidity	NTU	27.95±9.63	56.60±54.35	95.57±56.43	51.18±50.09	64.73±43.85
Temperature	°C	29.07±1.85	28.35±2.79	28.35±1.58	28.78±1.12	29.77±1.55
Bicarbonate	mg/L	147.70±86.91	222.00±111.79	103.76±49.76	161.19±169.42	110.80±45.15
Chloride	mg/L	226.24±125.98	173.56±81.89	107.44±32.69	118.23±43.52	136.38±77.65
Nitrate	mg/L	3.96±5.69	2.41±33.59	4.56±4.53	2.80±3.50	1.21±1.57
Sulphate	mg/L	19.58±9.29	9.03±6.93	12.03±11.57	8.79±8.18	24.22±30.74
Phosphate	mg/L	2.26±0.90	2.61±03.10	0.43±0.51	0.49±0.39	0.52±0.46
Copper	mg/L	0.28±0.38	0.17±0.24	0.11±0.16	0.30±0.34	0.12±0.12

**Note:** S<sub>1</sub>(July 2011-October 2011) S<sub>2</sub> (November.2011-March2012) S<sub>3</sub>( April 2012- October 2012)

S<sub>4</sub>( November 2012- March 2013) S<sub>5</sub>( April 2013- June 2013)

## DISCUSSION

The hydro chemistry of water in a river is altered by rainfall, temperature, weathering of rocks and anthropogenic impact which alter the quality and quantity of water in the river (Eneji 2010). In this study seasonal and monthly precipitation showed certain fluctuation in rainfall during the 24 months study period of this investigation. The comparison between different months and seasons showed that precipitation is attributed to the seasonal variation to the water quality. In the present research difference in rainfall pattern was evidence between months and seasons. Inland water bodies are characterized by unique hydrological features. In general, absolute and continuous vertical mixing of water in a river system is achieved due to the prevailing currents and turbulence. Consequently the water level continuously fluctuates between seasons and months. These fluctuations are quite unpredictable and account for the variation in the hydro chemistry of inland water bodies.

In this study, conductivity was reported to range from 9.90 - 1061.10  $\mu\text{S}/\text{cm}$  throughout the study period across the seasons at five Stations of River Benue at Makurdi. Comparison of the variation in conductivity showed that the changes in conductivity during the seasons and across the stations were significant (ANOVA- $P < 0.05$ ). The spatial and seasonal variation in conductivity in the river explained certain definite tendencies. The mean conductivity value at Station III was higher than the other Stations throughout the study period. Mean conductivity at Station II was the second highest during the time of this investigation. All the same Station IV was the lowest. There were significant variations in conductivity at the different Stations. These observations pointed out that conductivity is a highly variable in fresh waters. The higher mean values of conductivity at Station III ( $139.59 \pm 215.05$ ) and Station II ( $124.79 \pm 125.52$ ) may be attributed to the industrial waste discharged directly into the River at these two Stations. The seasonal variation showed that the conductivity values were increasing generally during the rainy as compared to the dry season. This result is evident to the fact that during the rainy season there is an increase in precipitation and hence increased runoff accounting for higher values of conductivity. Similar variation of conductivity in River Benue was reported (Eneji *et al.*, 2012). The findings of this study agrees with the result of a study of a tributary in Bonny estuary that reported higher values of conductivity during the rainy season as compared to the dry seasons  $15450 \pm 730 \mu\text{S}/\text{cm}$  and  $14610 \pm 760 \mu\text{S}/\text{cm}$  respectively (Davies 2013). Khan and Ishaq (2013) reported lower range in conductivity in River Yamuna which disagrees with the result of this study. Shinde *et al.* (2011) reported higher values of conductivity across seasons and at stations during their study in India.

During the entire period of this study the pH of surface water varied from 5.00 - 9.00. The variation in pH of surface waters in River Benue showed that pH was significant across seasons and stations throughout the study periods (ANOVA- $P < 0.05$ ). A plausible reason is evident that, the fluctuation in pH during the seasons and Stations were quite similar in River Benue at Makurdi during the study period. This is an indication that a more or less stable chemical quality exist throughout the water body. The mean pH value throughout the study period at different Stations showed slight variations downstream. This result could be attributed to the fact that the pH inducing factors are decreasing progressively downstream. A similar trend was observed in pH across the seasons as it showed slight variation. Nevertheless wet seasons were recorded with higher values of pH as compared to the dry season. This variation may be attributed to surface runoff during the rainy season. The variation in pH in this study disagrees with the result of an earlier study in River Benue at Makurdi that reported pH that ranged from: 6.40 - 7.79 (Eneji, *et al.*, 2012). Indabawa (2010) reported pH that ranged from: 7.2 - 7.3 in

River Challawa, Kano. Abowei (2010) reported pH in Nkoro River that ranges from 6.8 - 8.5. Ezekiel *et al.* (2011) reported pH in Sombreiro River that ranged from  $6.33 \pm 0.31$  -  $6.50 \pm 0.26$  and observed that the wet season pH ranged from 6.38- 6.52 while the dry season pH ranged from 6.10 - 6.45 which agree with the findings of this study that wet seasons pH are higher than dry season. However, the result of this study disagrees with that of Abowei (2010) whom reported higher values of pH in dry season as compared to wet season in Nkoro River Niger Delta. Similarly Davies (2013) reported higher values of pH during the dry months as compared to the wet months in Bonny estuary. The water samples of River Benue usually showed a narrow pH range and appeared to be buffered as was observed during the course of the study (Ziauddin *et al.*, 2013).

The total dissolved solids in River Benue during this study was reported to range from 6.81 - 521.33 mg/L. Comparison of variation in TDS indicates that the changes in TDS across the season were not significant (ANOVA- $P > 0.05$ ) whereas there was a significant difference in TDS across the different Stations (ANOVA- $P < 0.05$ ). Generally, the mean TDS at Stations III was observed to be higher than at the other Stations. The higher value of TDS in Station III and II may be due to the waste from the industries that are discharged directly into the River at these Stations. The insignificant difference in variations in TDS across seasons may be attributed to the fact that TDS in the River is stable and the seasons are not impacting on it. The result of this study disagrees with the result of an earlier study in River Benue that reported TDS that ranged from 17.1 - 70.00 mg/L (Eneji, *et al.*, 2012). David *et al.*, (2013) reported TDS that varied from 43.3-361.0 of two lacustrine wetlands of the upper Benue basin, Adamawa state Nigeria. This finding disagrees with the report of this study. The result of seasonal variation in TDS of this study showed that the TDS had a progressive increase during the rainy seasons as compared to dry season. This result disagrees with the result of an earlier study in River Benue that reported alternating increase and decrease of TDS in River Benue between seasons (Eneji, *et al.*, 2012). Jaji *et al.* (2007) reported alternating TDS values between rainy season and dry season in Ogun River. All the same higher TDS value of  $10500 \pm 440$  mg/L during the wet months as compared to dry months value of  $10190 \pm 530$  mg/L in Bonny estuary, Rivers state, Nigeria agrees with the findings of this study (Davies, 2013).

The result of total suspended solids in River Benue was determined to range from 5.00 - 410.00 mg/L during the study period of 24 months. The result of ANOVA showed that there was no variation in total suspended solids across seasons ( $P > 0.05$ ). Nevertheless, there was a significant change in total suspended solids across the different Stations (ANOVA- $P < 0.05$ ). However, the mean TDS value at Station II was the highest followed by Station III throughout the study period. The seasonal variation in TSS did not show a definite pattern across the seasons. All the same the lowest and highest TSS mean values were recorded in the rainy season. This could be that the TSS attributing factors are independent of season and more stable in River Benue during the course of this research. Eneji, *et al.* (2012) reported TSS in River Benue at Makurdi that varied from 20.00 - 892.00 mg/L which disagrees with the findings of this study. All the same, the finding of the seasonal trend of TSS in this study conforms to that of Eneji *et al.* (2012). Agbogu, *et al.* (2006) reported lower range of TSS  $18.36 \pm 2.06$  -  $29.33 \pm 3.29$  mg/L in surface waters in Zaria, Nigeria. Similarly, the seasonal variation in TSS of this study agrees with the result of TSS of a dam in India (Shinde *et al.*, 2011).

The colour of waters in River Benue during the study period ranged from 23.00 - 380.00 TCU. The variation of the colour of waters of River Benue at Makurdi during the seasons and at the Stations was significant (ANOVA- $P < 0.05$ ). The colour of waters at Stations II was reported

with the highest mean value among all the other Stations. This result may be attributed to the fact that colouring agent from the waste discharged into the River at this point was impacting on the colour of the waters. The result of seasonal variation in colour of the water of River Benue increased during the rainy season as compared to the dry season. TDS, TSS and colour in the River Benue during the study period showed similar changes. This could be that the factors that are responsible for the colour of the water are stable. The result of this study disagrees with the result of an earlier study on industrial effluents in Enugu state that reported colour that ranged from  $0.003 \pm 0.01 \pm 0.05 \pm 0.01$  TCU (Ani, *et al.*, 2011).

The turbidity of water in River Benue during the 24 months study period ranged from 3.00 - 258.00 NTU. This result disagrees with the findings that reported turbidity that ranged from 1.25-69.30NTU in two lakes in Adamawa state, Nigeria (David *et al.*, 2013). Comparison of variation in turbidity showed that the fluctuations during the seasons and at different Stations were significant (ANOVA-P<0.05). The result of the mean variation of turbidity at the different Stations showed that the highest value of turbidity was obtained at Station II and the lowest at Station V throughout the period of this investigation. The highest mean value of turbidity obtained at Station II may be attributed to the waste discharged into the River at this Station. The result generally showed that high values of turbidity were obtained during the rainy season as compared to the dry months which may be attributed to surface runoff that occurs in surface waters during the wet season. This finding conforms to the result of an earlier study in River Benue at Makurdi that reported higher values of turbidity during the wet seasons as compared to the dry season (Eneji, *et al.*, 2012). The result of this study also agree with the findings of a research in Ogun River that reported higher turbidity values during the rainy season which ranged from  $7.3 \pm 3.2$ - $61.0 \pm 29.5$ NTU as compared to the dry season that varied from  $9.3 \pm 7.0 \pm 25.3 \pm 5.0$  NTU (Jaji *et al.*, 2007).

The surface water temperature during the period of this research ranged from 23.00 - 33.50°C. Comparison of variation in of surface water temperature showed that the fluctuation during the seasons and across the stations throughout the study period was not significant (ANOVA-P>0.05). There were slight variation in surface water temperature at all the Stations during the study period. This may be due to the atmospheric temperature in Makurdi. All the same, the variation in temperature across the seasons was minimal. The surface water temperature reported in an earlier study in River Benue disagrees with the finding of this present study in River Benue (Eneji, *et al.*, 2012).

During the present study the bicarbonate ion concentration in the water samples ranged from 40.00 to 880.00mg/L. The seasonal variation of bicarbonate during the study period was significant (ANOVA-P<0.05). However, there was no significant difference at the different Stations throughout the period of the research. This could be that the factors contributing to the bicarbonates ion were stable in the course of the study. The spatial variation of the bicarbonate showed that Stations II had the highest mean concentration, while Station IV had the lowest. The highest concentration of bicarbonate at Station II may be attributed to the industrial waste from the brewery that is discharged directly into the River. The result of the seasonal variation of bicarbonate showed an increased in the bicarbonate concentration during the dry season as compared to the wet season. This could be that, during the dry season, there was a reduction in the water level in the River and hence more concentration of bicarbonate ion. The result of this study disagrees with the result of a study in River Tawi India that reported lower range of bicarbonate 86.00 - 146.40 mg/L (Mohan *et al.*, 2013).

The chloride of River Benue at Makurdi during the 24 months period of this investigation ranged from 35.47 - 546.03 mg/L. This result disagrees with the result of an earlier study in River Benue that reported chloride in the range of 0.4 - 2.41 mg/L (Eneji, *et al.*, 2012). The result of the spatial variation of chloride during the course of this study showed that the highest value of chloride was obtained at Station II and the lowest was at Station IV. The high mean value of chloride at Station II may be attributed to the brewery wastes that are dump directly into the River at this Station. The result of the seasonal variation of chloride concentration showed that during the study period, chloride concentration was increasing and decreasing between rainy and dry seasons. The result of the comparison of variation in chloride showed that the changes in chloride concentration during the seasons and across the different Stations were both significant throughout the study period (ANOVA-P<0.05). Generally, the chloride was high during the rainy season which is in agreement with the findings of other studies (Eneji *et al.*, 2012, Ishaq and Khan 2013, Mohan, *et al.*, 2013). However, the findings of some studies are in disagreement with the findings of this studies that reported higher values of chloride during the dry season as compared to the rainy season (Sharma *et al.*, 2013, Jaji *et al.*, 2007, Davies 2013).

The nitrate concentration in River Benue during the two years study time of this research ranged from 0.10 - 18.38 mg/L. The spatial variation of nitrate during the present investigation showed a progressive increase downstream from Stations: I - IV and then decreased at Station V. A plausible reason for this may that as move downstream the river course is steeper facilitate the movement of pollutant. The result of the seasonal variation showed an increase in the value of nitrate during the rainy season as compared to the dry season. The highest value of nitrate obtained at Station IV may be attributed to the anthropogenic impact from the animal waste from the abattoir that are dumped directly into the River. The indiscriminate disposal of human and animal waste that contributes to nitrate pollution is one of the greatest challenges of urbanization in developing nations (Jaji *et al.*, 2007). However, the result of this study is disagrees with the findings of an earlier study in River Benue that reported nitrate ion that ranged from 1.0 - 2.10 mg/L (Okayi *et al.*, 2011). Comparison of variation in nitrate showed that the fluctuations during the seasons were significant (ANOVA-P<0.05). All the same, there was no significant difference in nitrate across the different Stations (ANOVA-P>0.05). This result is evident in the fact that seasons are attributing to the nitrate while the Stations remains stable. The seasonal variation of this study is in agreement with the result of other studies that reported higher values of nitrate during the rainy season as compared to the dry season (Ademefemi *et al.*, 2007, Jaji *et al.*, 2007, Ishaq and Khan, 2013, Mohan *et al.*, 2013,).

During the period of this investigation, sulphate ranged from 0.80 – 90.00 mg/L. The result of the spatial changes of sulphate in River Benue during the study time indicate that the highest mean value of sulphate was obtained at Station III and the lowest was at Station V during the course of the study .The result of the seasonal variation indicates that the sulphate level increased during the rainy season as compared to the dry season .The seasonal trend depicts that sulphate concentration in River Benue in the course of the study was increasing during the rainy season and decreasing during the dry season. The highest value of sulphate at Station III may be attributed to the input of anthropogenic waste from the rice milling and processing company that are discharge directly into the River at this Station. Comparison of spatial and seasonal variation showed that the fluctuation in sulphate during the seasons was significant (ANOVA-P<0.05). All the same it was not significant at the different Stations (ANOVA-P>0.05). This may be due the fact that the seasons were contributing to the concentration of sulphate in River Benue while the Stations remain stable. The seasonal variation result of this

present investigation increased during wet season compared to the dry season. This result agrees with the findings of other studies (Shinde *et al.*, 2011, Mohan *et al.*, 2013.). However, this result disagrees with the findings of an earlier study a tropical lagoon that reported higher values of sulphate during the dry months as compared to the wet months, 113.5 mg/L and 35.5 mg/L respectively (Nwankwo *et al.*.,2010).

The phosphate concentration of River Benue during the 24 months study period ranged from 0.04 - 12.20 mg/L. This result disagrees with earlier studies in River Benue that reported phosphate that ranged from 1.20-19.0 mg/L and 0.07-0.20 mg/L respectively (OKayi *et al.*.,2011, Eneji *et al.*, 2012.). Phosphate values in surface waters are generally observed to be low (Nwankwo *et al.*.,2010). The spatial variation of phosphate indicates that the highest mean value of phosphate was obtained at Station III while the lowest was at Station V during the study period .The highest mean value of phosphate at Station III may be ascribed to phosphate run off from waste water discharged directly into the River at this Station.

The seasonal variation of phosphate result showed that phosphate was increasing during the dry season and decreasing during the wet season. This may be attributed to the reduced quantity of water in River during the dry season and a corresponding increase in the concentration of phosphate. This result however, disagrees with the findings of a study that reported higher value of phosphate in rainy season as compared to dry season (Jaji *et al.* ., 2007, Eneji *et al.*, 2012). All the same the result of this study agrees with the finding of study that reported higher value of phosphate during dry season as compared to rainy season (Ishaq and Khan, 2013). Comparison of variation in phosphate showed that the fluctuation during the seasons was significant (ANOVA - $P < 0.05$ ) while it was not significant across the stations (ANOVA- $P > 0.05$ ). This result may be attributed to the fact that during the season, the concentration of phosphate is neither increasing nor decreasing while the Stations remain stable.

The copper concentration in River Benue during the period of the present investigation ranged from 0.00 - 1.45mg/L. This result disagrees with the result of an earlier study in River Benue at Makurdi that reported copper that ranged from  $0.0448 \pm 0.07$  to  $0.696 \pm 0.02$  mg/L. (Eneji *et al.*, 2011). The result of the spatial variation during the period of the study showed that the highest concentration of copper  $0.31 \pm 0.34$  was obtained at Station II, while the lowest copper concentration of  $0.11 \pm 0.34$  was obtained at Station V. Industrial effluents and leachates from the brewery could be contributing to the elevated copper concentration at this Station . The seasonal variation of copper showed that the copper concentration was reducing during the rainy season. This results agrees with the findings of an earlier study in River Benue at Adamawa that reported higher values of copper in dry season (0.06 - 0.40 mg/L) than wet season (0.08 - 0.38 mg/L) during their study (Maitera *et al.*, 2011). Jaji *et al.* (2007) also reported higher values of copper during the dry season as compared to wet season in Ogun River. The higher value of copper during the dry season may be due to the reduced water quantity and increased concentration. Comparison of variation in copper showed that the fluctuation in copper during all the seasons were significant (ANOVA- $P < 0.05$ ). However, there was no significant difference across different Stations (ANOVA -  $P > 0.05$ ). This may due to the fact that the seasons the impacting on copper level while the stations are stable.

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