

Seasonal variation of reservoir water quality: A case study of Kubanni reservoir, Zaria, Nigeria

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Abstract

Background: Reservoirs serve as fishing and domestic water resources for the people living around the catchment area. However, natural activities threaten the water quality, therefore, constant and proper monitoring of the reservoir is necessary. This study aimed to examine seasonal variation in water quality parameters of Kubanni reservoir, Zaria, Nigeria.

Methods: Water quality data of Kubanni reservoir, Zaria, Nigeria, for 7 years (January 2014 to December 2020) were collected and analyzed to understand the seasonal variation. Ten water quality parameters including pH, turbidity, electrical conductivity (EC), temperature, total dissolved solids (TDS), dissolved oxygen (DO), chloride (Cl⁻), total Iron, nitrate (NO³⁻), and manganese (Mn) were analyzed. The data were analyzed using Kolmogorov-Smirnov test to select the probability distribution which provides the best fit by EasyFit software. The functions included Weibull, Exponential, Fréchet, Gamma, Lognormal, and Normal. Seasonal variation was determined using Spearman's rank-order correlation.

Results: The results showed that pH, EC, temperature, TDS and NO³⁻ approach the Weibull distribution. Turbidity and total Iron approach the Fréchet distribution. Mn approaches the normal distribution, while DO and Cl approach the Gamma distribution. The output of non-parametric Spearman's correlation coefficient and Spearman's statistical criterion indicates a significant difference at 5% significance level between the pH and total Iron values recorded in both seasons. This suggests that season has an effect on the concentration of pH and total Iron.

Conclusion: Out of the 10 parameters examined, pH and total Iron are climatologically influenced.

Keywords: Seasons, Water quality, Iron, Normal distribution, Nigeria

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Introduction

Water quality is one of the most important factors that must be taken into account while assessing the sustainability of the development of a region (1). Water quality is a critical factor that influences human health and agricultural production in semi-humid and semi-arid areas (2). Seasonal variation influences the water quality of reservoirs (3, 4). Seasonal variation in surface water quality must be considered when creating a water quality management program (5). The pollution of water bodies normally results from pathways including stormwater runoff, discharge from ditches and creeks, vadose zone leaching, groundwater seepage, and atmospheric deposition. These pathways are also seasonal-dependent. Sahana and Danbul detected high concentrations of total suspended solids (TSS) and chemical oxygen demand (COD) parameters during rainy season compared to dry season (6). According to the study of Hun-Kyun, rainfall events after a long-term dry season accelerate water quality degradations since pollutants may be accumulated on the surface areas during dry season (7). In contrast, degradations of river water quality which experienced several previous heavy rainfall events are likely to be less. Furthermore, Yu et al reported that the relationship between water quality

variables and proportion of different land uses were weaker in the rainy season than that in the dry season (8). Dry season has more effects on the quality or concentration of surface water than the rainy season.

Poor water quality monitoring is linked to transmission of diseases and cost of water treatment, which substantially impairs the beneficial uses of water (1). Kubanni reservoir serves as fishing and domestic water resources for the people living around the catchment area. However, natural activities threaten the water quality, therefore, constant and proper monitoring of the reservoir is necessary. According to the study of Moridi et al, water in reservoir can be affected by point and non-point sources of contamination (9). In addition, the physical, chemical and biological conditions of stored water may be worsened by storage in reservoir (9). UNEP reported that monitoring of freshwaters is the first action to be taken to prevent the increase of pollution, and also, to restore polluted water bodies (10).

Many studies have been done in details to check the quality of surface water. Antonopoulos et al examined the time series of monthly values (1980-1997) of water quality parameters and the discharge using statistical methods, the existence of trends and the evaluation of the best fitted models were performed. In



addition, the relationships between concentration and loads of constituents both with the discharge were also examined. Boxplots were used for summarizing the distribution of a data set. The chi-square and Kolmogorov-Smirnov tests were used to select the theoretical distribution, which best fitted the data. Simple regression was used to examine the concentration-discharge and the load-discharge relationships. Spearman's criterion was used to examine the data for discharge, electrical conductivity (EC), dissolved oxygen (DO), sulphate, sodium, potassium, and nitrate (NO_3^-) on which temporal trend analysis was performed. The results showed that seasonal variations in stream water chemistry are strongly related to discharge variations (11). Gocic and Trajkovic monitored the data of 12 water quality parameters daily at the Nis station on the Nisava River from 2000 to 2004. Trend analysis was performed on monthly, seasonal, and annual time series using the Mann-Kendall test, the Spearman's rho test, and the linear regression at the 5% significance level. The monthly results showed that significant trends were found only in pH, total hardness, Ca and SO_4 data while the results in seasonal series indicated that the significant trends were detected in pH, total hardness, Cl, Ca, and SO_4 data (12). Sentas et al (13) assessed water level, EC, active acidity, water temperature, air temperature, and DO data in River Nestos, Pagoneri, from 2004 to 2007. The application of the trend test with a best-fit straight line led to the following conclusions. The water level showed a negative trend, EC showed a rising trend (positive), while pH showed conflicting results (positive and negative). The negative trend means that a reduction in the water level was observed over time. The EC parameter showed a rising trend. For the DO parameter, the estimated trend was negative. For pH, there was neither positive nor negative trend, indicating that there was no increase or decrease in pH. However, the slope value was zero, which made the results draw conflicting conclusions. In order to obtain more accurate conclusions, the application of the Augmented Dickey-Fuller test was regarded necessary. For the water and air temperature, the linear trend was estimated to be negligible. That is, temperatures do not show any increase or decrease over time. Vachhani et al used Mann-Kendall trend and Sen's slope estimator tests to ascertain the trend in monthly time series of 14 water quality parameters from 1990-2013 (23 years). The results showed significant trends in calcium (Ca^{2+}), chloride (Cl^-), fluoride (F^-), ammonia-nitrogen ($\text{NH}_3\text{-N}$), and nitrate nitrogen ($\text{NO}_3\text{-N}$) at all 4 stations in the basin. The study also revealed that the seasonal influences and anthropogenic activities like consumption of fertilizer in agricultural sector and untreated sewage disposal could be the factors contributing to the increasing trend of nutrient-related parameters like pH, $\text{NO}_3\text{-N}$, and biochemical oxygen demand (14).

Researches have shown that identifying the trend and periodicity of the observed data is a meaningful way to study the water quality parameter variation (15-17). Hence, Gocic and Trajkovic concluded that the trend analysis of water quality data is an essential task for understanding the changes of water quality parameters, predicting streams, and monitoring water quality (12). Non-parametric statistical tests such as Mann-Kendall's test, Sen's slope estimator, and Spearman's Rho test have been used by various researchers to determine the trends in water quality (11, 12, 14, 18, 19). The Spearman's Rho test is a non-parametric statistical test used to determine if there is a significant relationship or correlation between two data sets (11). The test also measures how strong any correlation is and its polarity (positively or negatively correlated).

Water quality data can be analyzed using Spearman's rho

test. These data may contain missing values that can have a significant effect on the results (14). The most common methods to fill in the missing values are their substitution with either; the series mean, the mean or median of a part of the time series values i.e. before and after the gap (mean or median of nearby points), linear interpolation or linear trend at point (13). Linear interpolation method has been considered as a suitable method to complete missing values (20, 21). According to the study of Vachhani et al, to minimize the effect of missing data, value of particular month are filled using the average value of three-year data of the same month (14). This approach was adopted for the present study. Hence, the aim of this research was to analyze the seasonal variation of water quality parameters using Spearman's rank-order correlation coefficient and Spearman's statistical criterion.

Materials and Methods

Study area

The Samaru sub-catchment (Kubanni drainage basin) originates in the confines of Ahmadu Bello University Main Campus, South West of its Teaching Hospital at Shika as a trench crossing undulating agricultural land. The Kubanni River takes its course from the Kampagi Hills in Shika near Zaria and flows in a south east direction through Ahmadu Bello University and southwest direction into River Galma. The Kubanni river flows through several research institutions such as Ahmadu Bello University Teaching Hospital, Ahmadu Bello University main campus, Centre for Energy Research and Training, Institute of Agricultural Research, Nigeria College of Aviation Technology as well as several rural and urban settlements such as Samaru, Zango, Palladan, Kwangila, GRA, PZ, Tudun Jukun, Tudun Wada, and Gyelesu before draining into the Kubanni Reservoir. The Kubanni River was dammed by the authorities of Ahmadu Bello University, Zaria in 1973 at about 7.25 km from the source to provide water supply to the growing University community (22). The stretch of the reservoir falls between Latitude $11^{\circ}08'21.57''\text{N}$ to $11^{\circ}07'54.86''\text{N}$ and Longitude $7^{\circ}38'57.44''\text{E}$ to $7^{\circ}39'28.67''\text{E}$.

The climate of Nigeria is strongly influenced by the Equatorial Maritime and Tropical Continental air masses (23). The boundary between these two is known as the Intertropical Convergence Zone (ITCZ). The Equatorial Maritime air mass is characterized by south-westerly winds, which approaches the land off the Gulf of Guinea. Rainfall in Zaria is derived from this moisture-laden air mass with a long history of movement over the Atlantic Ocean (24). The Tropical Continental air mass is that of the dry north easterly wind known as Harmattan. In other words, the climate of the studied area is very much affected by movement of the ITCZ. The rainy season in Zaria and its environment is normally in the period of May to October, when the ITCZ has reached the northern part of Nigeria. The dry season, usually accompanied with high evaporation rate is from November to April when the North Easterly wind covers the whole of the northern part of Nigeria (24). The mean annual rainfall can be as high as 2000 mm in rainy years and as low as 500 mm in dry years, but with a long-term rainfall average of 1000 mm (25, 26). The mean annual temperature is about 24.5°C (25).

Data collection

Monthly data of 10 water quality parameters from January 2014 to December 2020 were collected for analysis from Ahmadu Bello University Water Treatment Plant. The parameters included pH, turbidity, EC, temperature, total dissolved solids

(TDS), DO, Cl⁻, total Iron, nitrate (NO³⁻), and manganese (Mn). The geographical location of the sampling location was at latitude 11° 8' 26.55"N and longitude 7° 39' 20.91"E. Missing data were corrected using the average value of 3-year data of the same month (14). The parameters were tested according to scheduled sampling frequency for centralized system recommended by Nigerian Standard for Drinking Water Quality (NSDWQ). Seasonal classifications were based on dry seasons (November, December, January, February, March, and April) and rainy seasons (May, June, July, August, September, and October) (27).

Fitting water quality data to a probability distribution

To select the distribution providing the best fit, probability distribution function was examined using EasyFit software. The functions were Weibull, Exponential, Fréchet, Gamma, Lognormal, and Normal. Kolmogorov-Smirnov test was used to select the distribution, which fits the data best.

Trend analysis

Seasonal variation was determined using Spearman's rank-order correlation coefficient described in Eq. (1).

$$R_{sp} = 1 - \frac{6 \sum_{i=1}^n (D_i D_i)}{n(n^2 - 1)} \quad (1)$$

Where n is the total number of values in each time-series, i is the chronological order number, and D_i is the difference between rankings. The null hypothesis, H_0 : $R_{sp} = 0$ (there is no difference) is against the alternate hypothesis, H_1 : $R_{sp} < \text{or} > 0$ (there is a difference).

To detect the existence of significant seasonal change, the non-parametric Spearman's statistical criterion, t_s which has Student's t-distribution with $n-2$ degrees of freedom was used. The Spearman's statistical criterion, t_s , is described in Eq. (2).

$$t_s = R_{sp} \left[\frac{n-2}{1-R_{sp}^2} \right]^{0.5} \quad (2)$$

Where t_s has Student's t-distribution. At a significance level of 5%, the time-series has no significant seasonal variation if: $t\{v, 2.5\% \} < t_s < t\{v, 97.5\% \}$ (3)

Results

According to the Kolmogorov-Smirnov test, pH, EC,

temperature, TDS, and Nitrate approach the Weibull distribution with test statistic values of 0.09346, 0.06052, 0.1074, 0.04768, and 0.05669, respectively. Turbidity and total Iron approach the Fréchet distribution with test statistic values of 0.11664 and 0.13801, respectively. Mn approaches the normal distribution with test statistic value of 0.15201, while DO and Cl⁻ approach the Gamma distribution with test statistic values of 0.09587 and 0.09366, respectively.

pH

The pH values ranged from 5.03 to 7.5 during the dry seasons and from 3.92 to 7.2 during the rainy seasons. The values of Spearman's correlation coefficient and Spearman's statistical criterion were 0.4482 and 3.1710, respectively at 5% significance levels for seasonal variation, which for $n=42$ (3.5 years), is: $t\{42, 2.5\% \} < t_s < t\{42, 97.5\% \}$, where: $t\{42, 2.5\% \} = -2.02$ and $t\{42, 97.5\% \} = 2.02$. According to Figure 1, the pH values during the dry seasons were higher than the rainy seasons.

Turbidity

The turbidity values during the dry seasons ranged from 12.9 to 17372 NTU and from 22.7 to 9172 NTU during the rainy seasons. The values of Spearman's correlation coefficient and Spearman's statistical criterion were 0.0197 and 0.1246, respectively at 5% significance levels for seasonal variation, which for $n=42$ (3.5 years), is: $t\{42, 2.5\% \} < t_s < t\{42, 97.5\% \}$, where: $t\{42, 2.5\% \} = -2.02$ and $t\{42, 97.5\% \} = 2.02$. According to Figure 2, turbidity showed obvious seasonal variations between values of dry and rainy seasons early in the time-series, and subsequently, remained relatively constant.

Electrical conductivity

The EC values during the dry seasons ranged from 61.6 to 156.4 $\mu\text{S}/\text{cm}$ and from 21.5 to 139 $\mu\text{S}/\text{cm}$ during the rainy seasons. The values of Spearman's correlation coefficient and Spearman's statistical criterion were -0.0469 and -0.2969, respectively at 5% significance levels for seasonal variation, which for $n=42$ (3.5 years), is: $t\{42, 2.5\% \} < t_s < t\{42, 97.5\% \}$, where: $t\{42, 2.5\% \} = -2.02$ and $t\{42, 97.5\% \} = 2.02$. According to Figure 3, the EC values were higher during the dry seasons than the rainy seasons.

Temperature

The temperature values during the dry seasons ranged from 17.7 to 32.3°C and from 24.3 to 39.5°C during the rainy

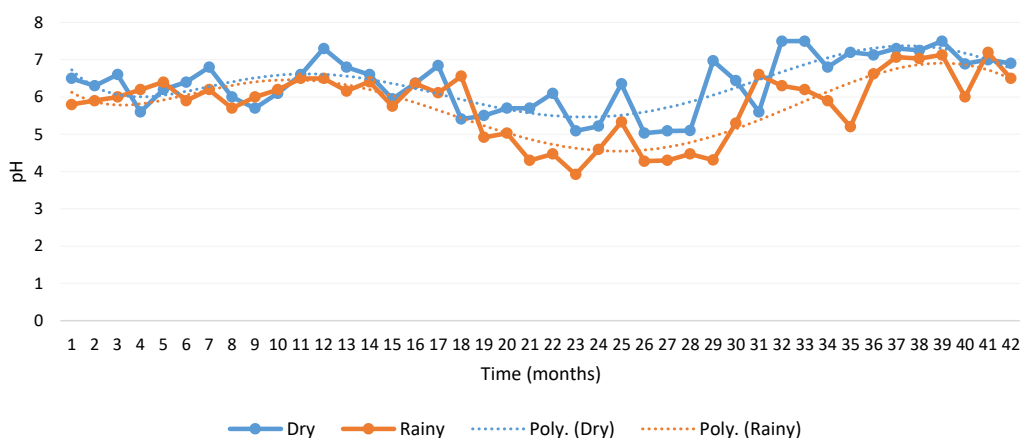


Figure 1. Seasonal variation of pH.

seasons. The values of Spearman's correlation coefficient and Spearman's statistical criterion were -0.0857 and -0.544, respectively at 5% significance levels for seasonal variation, which for $n=42$ (3.5 years), is: $t_{\{42, 2.5\}} < t_i < t_{\{42, 97.5\}}$, where: $t_{\{42, 2.5\}} = -2.02$ and $t_{\{42, 97.5\}} = 2.02$. According to Figure 4, water temperature during the rainy seasons was slightly higher.

Total dissolved solids

The TDS values during the dry seasons ranged from 30.1 to 93.7 mg/L and from 13.24 to 83.7 mg/L during the rainy seasons. The values of Spearman's correlation coefficient and Spearman's statistical criterion were 0.02 and 0.1265, respectively at 5% significance levels for seasonal variation, which for $n=42$ (3.5 years), is: $t_{\{42, 2.5\}} < t_i < t_{\{42, 97.5\}}$, where: $t_{\{42, 2.5\}} = -2.02$ and $t_{\{42, 97.5\}} = 2.02$. According to Figure 5, the TDS values

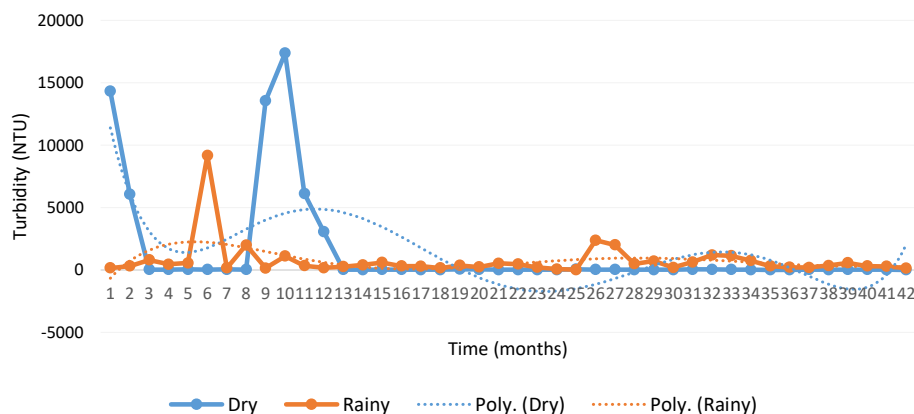


Figure 2. Seasonal variation of turbidity.

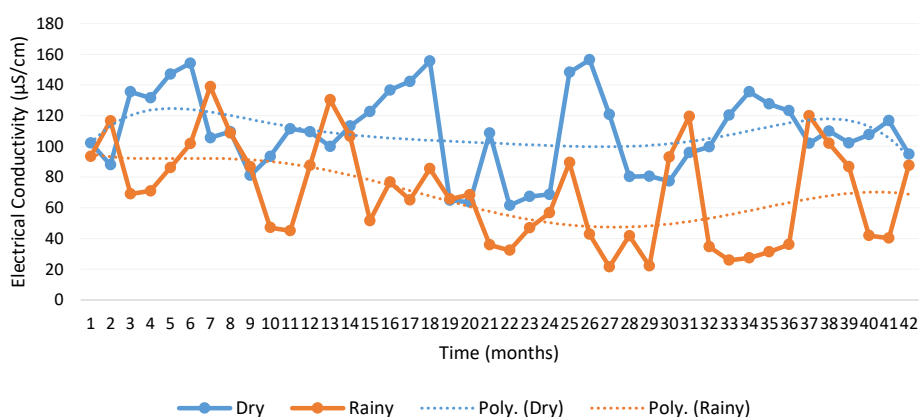


Figure 3. Seasonal variation of electrical conductivity.

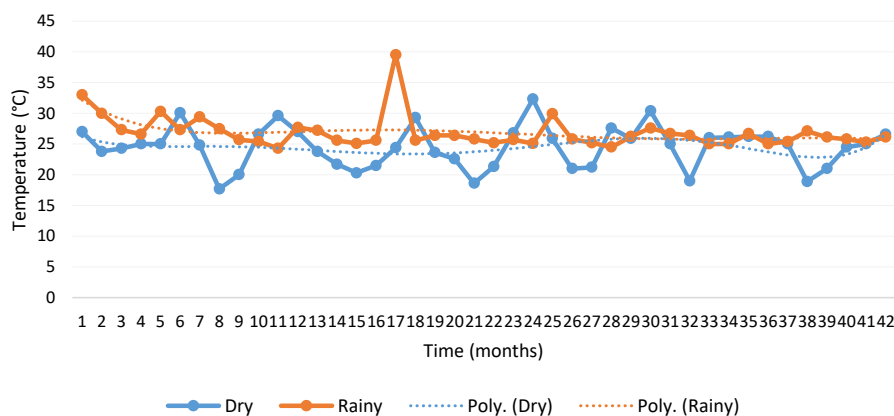


Figure 4. Seasonal variation of temperature.

were higher during the dry seasons than the rainy seasons.

Dissolved oxygen

The DO values during the dry seasons ranged from 0.4 to 3.5 mg/L and from 0.4 to 3.1 mg/L in the rainy seasons. The values of Spearman's correlation coefficient and Spearman's statistical criterion were -0.0652 and -0.4132, respectively at 5% significance levels for seasonal variation, which for $n=42$ (3.5 years), is: $t_{\{42, 2.5\}} < t < t_{\{42, 97.5\}}$, where: $t_{\{42, 2.5\}} = -2.02$ and $t_{\{42, 97.5\}} = 2.02$. According to Figure 6, the DO values

show no evident seasonal variations over the period.

Chloride

The Cl^- values during the dry seasons ranged from 27.5 to 128 mg/L and from 22 to 120 mg/L in the rainy seasons. The values of Spearman's correlation coefficient and Spearman's statistical criterion were 0.2635 and 1.7276, respectively at 5% significance levels for seasonal variation, which for $n=42$ (3.5 years), is: $t_{\{42, 2.5\}} < t < t_{\{42, 97.5\}}$, where: $t_{\{42, 2.5\}} = -2.02$ and $t_{\{42, 97.5\}} = 2.02$. According to Figure 7, the Cl^- values were slightly

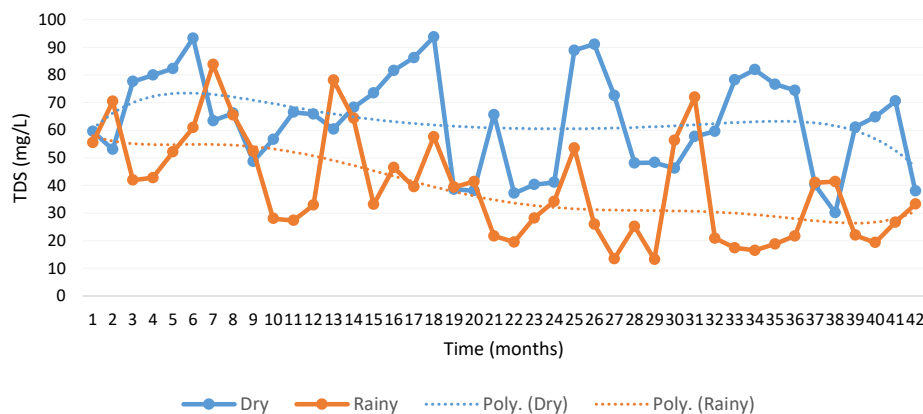


Figure 5. Seasonal variation of total dissolved solids.

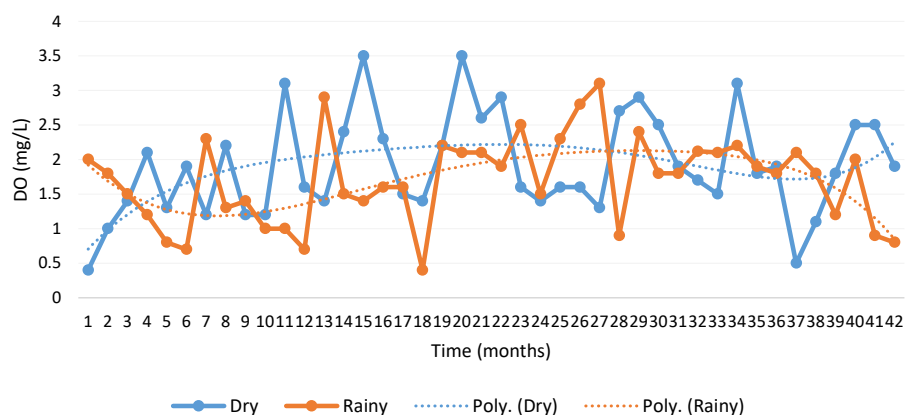


Figure 6. Seasonal variation of dissolved oxygen.

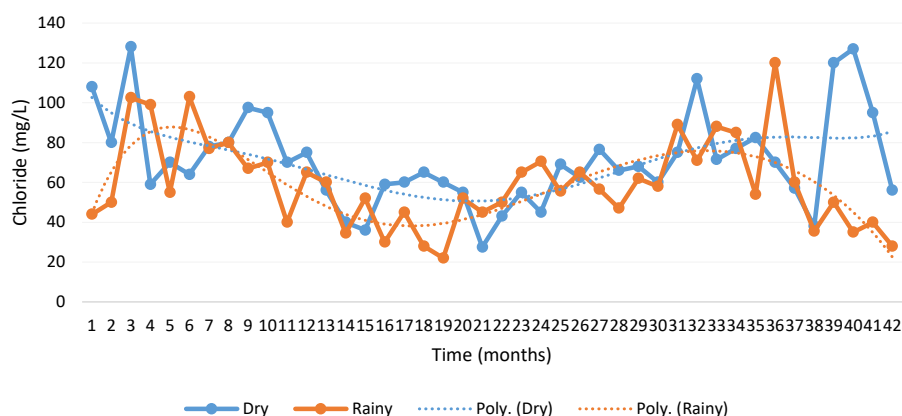


Figure 7. Seasonal variation of chloride.

higher in the dry seasons than the rainy seasons.

Total iron

The total Iron values during the dry seasons ranged from 0.2 to 3.67 mg/L and from 0.19 to 3.17 mg/L during the rainy seasons. The values of Spearman's correlation coefficient and Spearman's statistical criterion were 0.3683 and 2.5054, respectively at 5% significance levels for seasonal variation, which for $n=42$ (3.5 years), is: $t_{\{42, 2.5\}} < t_i < t_{\{42, 97.5\}}$, where: $t_{\{42, 2.5\}} = -2.02$ and $t_{\{42, 97.5\}} = 2.02$. According to Figure 8, the total Iron values were higher during the rainy seasons than the dry seasons over the period.

Nitrate

The nitrate values during the dry seasons ranged from 6.34 to 39 mg/L and from 9.2 to 28.1 mg/L during the rainy seasons. The values of Spearman's correlation coefficient and Spearman's statistical criterion were -0.0863 and -0.5479, respectively at 5% significance levels for seasonal variation, which for $n=42$ (3.5 years), is: $t_{\{42, 2.5\}} < t_i < t_{\{42, 97.5\}}$, where: $t_{\{42, 2.5\}} = -2.02$ and $t_{\{42, 97.5\}} = 2.02$. According to Figure 9, the nitrate values showed no obvious seasonal variations over the period.

Manganese

The Mn values during the dry seasons ranged from 0.01 to 0.3 mg/L and from 0.01 to 0.2 mg/L in the rainy seasons. The values of Spearman's correlation coefficient and Spearman's statistical

criterion were 0.2446 and 1.5954, respectively at 5% significance levels for seasonal variation, which for $n=42$ (3.5 years), is: $t_{\{42, 2.5\}} < t_i < t_{\{42, 97.5\}}$, where: $t_{\{42, 2.5\}} = -2.02$ and $t_{\{42, 97.5\}} = 2.02$. According to Figure 10, the Mn values showed no obvious seasonal variations over the period.

Discussion

pH

Spearman's correlation coefficient and Spearman's statistical criterion suggest that the reservoir pH is climatologically influenced (season has an effect on the concentration of pH) (27). Significant variation in the pH of Kubanni reservoir is possibly due to atmospheric pollutants, particularly oxides of sulphur and nitrogen caused by anthropogenic events. These can cause precipitation to become acidic when converted to sulphuric and nitric acids (28). Hence, the rainfall might have reduced the pH of the reservoir during the rainy seasons. This has been observed in similar water bodies in Nigeria by several studies (27, 29, 30).

Turbidity

Spearman's correlation coefficient and Spearman's statistical criterion indicate that there was no significant difference at 5% significance level between the turbidity values recorded in both seasons, which is inconsistent with the results of similar studies (27, 31, 32). Turbidity may be higher during the rainy seasons as a result of runoff. Runoff particles from agricultural fields,

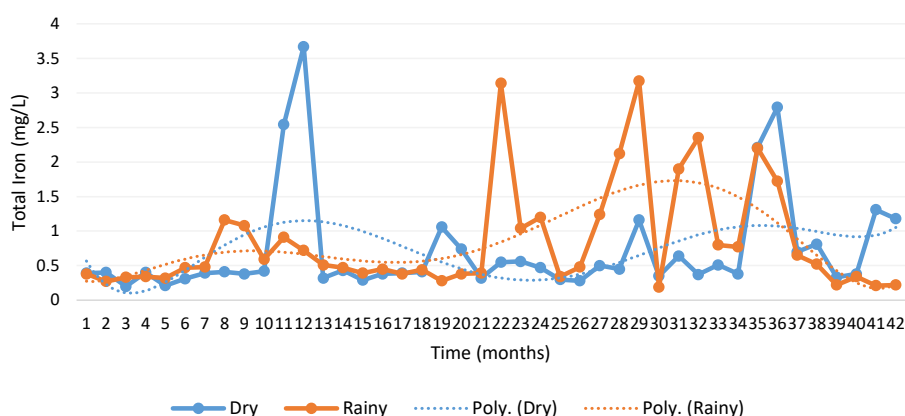


Figure 8. Seasonal variation of total iron.

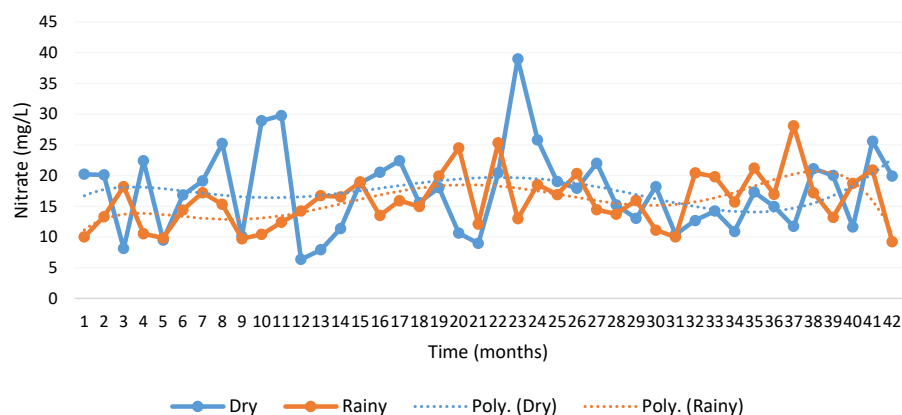


Figure 9. Seasonal variation of nitrate.

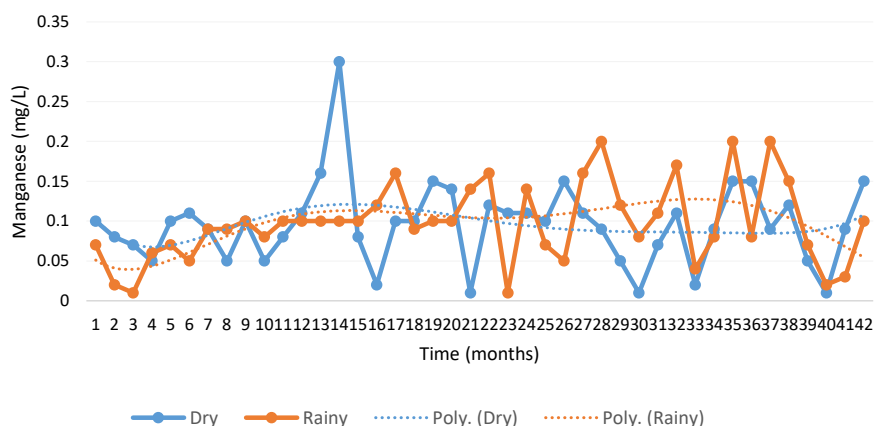


Figure 10. Seasonal variation of manganese.

drainages and unpaved urban land are easily washed from the soil. This runoff with its associated debris finally flows into the river thereby causing the river water to be highly turbid during rainy seasons (27). Nonetheless, the presence of turbidity during dry seasons despite the absence of runoff might be caused by in-stream activities like dredging, which occurred between 2014 and 2016 (33). In addition, water level in reservoirs is usually low during the dry seasons. Hence, other in-stream activities such as rowing of canoes by fishermen might have stirred up bottom sediments, which also increases the turbidity.

Electrical conductivity

Spearman's correlation coefficient and Spearman's statistical criterion indicate that there was no significant difference at 5% significance level between the EC values recorded in both seasons. Dilution of the concentrated dissolved solids by precipitation, which occurred during the rainy seasons, might be the reason for the lower EC values recorded during the rainy seasons (27). This can be inorganic dissolved solids such as Cl^- , nitrate, sulphate, and phosphate anions or sodium, magnesium, calcium, iron, and aluminum cations (34, 35). The seasonal variation of EC (Figure 3) is similar to that of TDS (Figure 5) and slightly similar to that of Cl^- (Figure 7). This could be because EC is a linear function of TDS and Cl^- ion (36, 37).

Temperature

Spearman's correlation coefficient and Spearman's statistical criterion indicate that there was no significant difference at 5% significance level between the temperature values recorded in both seasons. Atmospheric humidity is usually less during dry seasons (particularly during harmattan) than rainy seasons. This might have caused more water molecules on the surface of the reservoir to evaporate during the dry seasons than rainy seasons (27). The higher the evaporation rate, the lesser the water temperature (cooling effect of evaporation) during dry seasons (27).

Total dissolved solids

Spearman's correlation coefficient and Spearman's statistical criterion indicate that there was no significant difference at 5% significance level between the TDS values recorded in both seasons. Some studies reported lower TDS values during the dry season (38, 39), which is inconsistent with the results of other studies (27, 40-42) that reported high concentrations of TDS in the dry seasons. Surface waters naturally contain some

dissolved solids regardless of the season due to the dissolution and weathering of rocks and soils (34). Surface runoff due to precipitation (typically during rainy seasons) is a major source of TDS in water bodies. Although statistically insignificant, high TDS in the dry seasons might be linked to the consequence of higher evaporation rate in the dry seasons caused by solar heating and low humidity (43). TDS exist as solutes in solvent (water), thus, as the evaporation rate of the solvent (water) surges in the dry seasons, the concentration of the solutes (TDS) in the surface water rises similarly (27).

Dissolved oxygen

Spearman's correlation coefficient and Spearman's statistical criterion indicate that there was no significant difference at 5% significance level between the DO values recorded in both seasons. The DO concentration was below the NSDWQ and WHO prescribed limit (>4.0 mg/L) during the entire period. This may be due to salinity. Salinity is an essential factor in determining the amount of oxygen in water (44). This is because as the amount of dissolved salt in water rises, the amount of oxygen the water can hold declines and vice versa (44). Likewise, organic pollutants in surface water regularly reduce the DO content because bacteria consume and utilize the existing oxygen to oxidize these organics.

Chloride

Spearman's correlation coefficient and Spearman's statistical criterion indicate that there was no significant difference at 5% significance level between the Cl^- values recorded in both seasons. Some studies also reported lower concentrations of Cl^- during rainy seasons compared to dry seasons in surface water (45, 46). Dilution triggered by precipitation during rainy seasons may cause lower concentrations of Cl^- in the rainy seasons compared to dry seasons. Tchobanoglus et al stated that the human excreta produced per person per day contain about 6 g of Cl^- (47). High Cl^- levels during the rainy seasons may also be attributed to runoff which carries waste (excreta) into water bodies. In addition, irrigation and rising of groundwater tables has been reported as one of the main causes of Cl^- in agricultural watersheds, predominantly in the arid and semi-arid regions of the world where crop production consumes large quantities of water (48). This is because crops absorb only a fraction of the salt in irrigation water, consequently, making soil water to be more saline or salty, which usually leached out through interflow and

end up in the river (49). Similarly, the practice of excessive use of inorganic fertilizers to improve soil fertility by farmers might be another reason for the presence of Cl^- in the agricultural watershed (50).

Total iron

Spearman's correlation coefficient and Spearman's statistical criterion indicate a significant difference at 5% significance level between the total iron values recorded in both seasons. This suggest that the reservoir total Iron is climatologically influenced (season has an effect on the concentration of total iron) (27). The lower concentrations of total iron during the rainy seasons than the dry seasons could be attributed to the dilution effect of precipitation experienced during the rainy seasons (27). High aeration initiated by high stream flow rates and runoff into the reservoir probably due to high DO during the rainy seasons reduces the total iron (51). High concentrations of total Iron during the dry seasons may be due to re-suspension from polluted sediments (52).

Nitrate

Spearman's correlation coefficient and Spearman's statistical criterion indicate that there was no significant difference at 5% significance level between the nitrates value recorded in both seasons. Higher concentrations of nitrate during dry seasons compared to rainy seasons have earlier been observed in similar studies (45, 53, 54). Lower nitrate values in the rainy seasons could be due to the effect of precipitation on pollutant dilution (27). Also, during rainy seasons, not all the precipitation on a watershed flows as surface runoff into reservoirs. Some of the rainfall that is sub-surface runoff or interflow, is leached into the soil and moves laterally without joining the water table, to the reservoirs. Nonetheless, another proportion of the rainfall known as base-flow infiltrate deep into the soil and meet the water table before flowing into reservoirs. The movement of water in this type of runoff (base-flow) is very slow before entering the reservoirs. In percolated water, Nitrate is usually caused by the oxidation of nitrogen compounds by soil bacteria and it moves freely with groundwater flow (55, 56). Hence, higher values of NO_3^- during the dry seasons could also be caused by deep infiltrated waters (base-flow) that were contaminated with nitrogen compounds leached into the reservoir during the dry seasons.

Manganese

Spearman's correlation coefficient and Spearman's statistical criterion indicate that there was no significant difference at 5% significance level between the Mn values recorded in both seasons. Similar studies in other Nigerian rivers have reported higher concentrations of Mn during dry seasons (30, 54, 57-59). Lower concentrations of Mn in rainy seasons compared to dry seasons could be attributed to the dilution effect of precipitation during rainy seasons (27). Also, the natural presence of Mn in rocks could be a cause of presence of high concentrations of Mn in the reservoir (34). High concentrations of Mn during the dry seasons can lead to bioaccumulation in the reservoir (27).

Conclusion

According to the Kolmogorov-Smirnov test, pH, EC, temperature, TDS, and nitrate approach the Weibull distribution with test statistic value of 0.09346, 0.06052, 0.1074, 0.04768, and 0.05669, respectively. Turbidity and total iron approach the Fréchet distribution with test statistic values of 0.11664 and 0.13801,

respectively. Mn approaches the normal distribution with test statistic value of 0.15201, respectively, while DO and Cl^- approach the Gamma distribution with test statistic values of 0.09587 and 0.09366, respectively. Out of the 10 parameters examined, there was significant seasonal variations at 5% significance level between the pH and total Iron values (Spearman's statistical criterion of 3.1710 and 2.5054, respectively), which suggest that pH and total Iron parameters are climatologically influenced.

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Ethical issues

The research was approved by a group of experts from the Department of Water Resources and Environmental Engineering, Ahmadu Bello University, Nigeria, on September 2, 2021.

Competing interests

The authors declare that they have no conflict of interests.

Authors' contributions

All authors were involved in every aspect of the study.

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