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Physico-Chemical Assessment of River Benue to Determine Pollution Levels Using Chemometric Models

U.U. Egereonu[1,*], J.C. Ike[2], R.U. Iwuagwu[3], S.K. Egereonu[4], C. Onwuka[5], J.C. Egereonu[6], N.J. Okoro[7], U.L.Onu[8], V.C. Eze[9], B.Okenyi[10]

Abstract

The effects of pollution on water have been reviewed. This study is aimed at determining the level of pollution of the River Benue, with the view of assessing its use as potable water. Different analytical techniques including titrimetry, gravimetry, potentiometry, and spectrophotometry were used for the study. The total hardness gave (22.28 mg/L and 41.87 mg/L) for dry and rainy season respectively. Electrical conductivity gave (91.35 mg/L and 54.10 mg/L) for rainy and dry seasons respectively. The Total dissolved solids gave (76.02 mg/L and 32.31 mg/L) respectively in the rainy and dry season showing the presence of more soluble and dissolved ions in the rainy season. Dissolved oxygen gave (3.18 m/L & 3.72 mg/L) for rainy and dry season respectivley. For phosphate (0.85 mg/L & 0.73 mg/L) were measured in dry and rainy season respectively. Sodium gave (2.95 mg/L & 2.78 mg/L) for dry and rainy seasons. While calcium gave (2.07 mg/L & 1.57 mg/L) for both dry and rainy seasons. While chemical oxygen demand gave (114.37 mg/L &84.97 mg/L) for rainy and dry season. Biochemical oxygen demand were (24.87 mg/L & 25.63 mg/L) for rainy and dry seasons and were above the recommended drinking water standard for world health organization (WHO). Higher level of lead (0.00865 mg/L & 0.00281 mg/L) for both dry and rainy season and copper (1.24 mg/L & 0.9734 mg/L) for both dry and rainy seasons were found in the water which is harmful to health of the aquatic ecosystem and the communities utilizing the water for domestic purposes. The mean values of all the parameters were correlated using Pearson Product Moment Correlation Coefficient. The value of r is 0.91. This implies that the status of the river as it concerns its potability is the same, irrespective of the little fluctuation that might be observed in the different season. MATLAB and ANN were also used for the analysis of River Benue.

***Author for Correspondence**
U.U. Egereonu
E-mail: uegeronu@gmail.com

[1]Professor, Deptartment of Chemistry, Federal University of Technology Owerri, Nigeria
[2]Assistant Lecturer, Deptartment of Chemistry, Federal University of Technology Owerri, Nigeria
[3]Assistant Lecturer, Deptartment of Chemistry, Rivers State University of Science and Technology, Port Harcourt, Nigeria
[4]Assistant Lecturer, Deptartment of Information Technology, Federal University of Technology Owerri, Nigeria
[5]Lecturer, Deptartment of Chemistry, Rhema Universiy, Aba, Nigeria
[6]Assistant Lecturer, Department. of Geoscience, Federal University of Technology Owerri, Nigeria
[7]Lecturer, Deptartment of Chemistry, Univerisity of Agriculture and Environmental Sciences, Umuagwo, Imo State, Nigeria
[8]Lecturer, Deptartment of Chemistry, Federal University of Technology Owerri, Nigeria
[9]Lecturer, Deptartment of Chemistry, Univerisity of Agriculture and Environmental Sciences, Umuagwo, Imo State, Nigeria
[10]Lecturer, Department of Chemistry, University of Health Sciences, Makurdi, Benue State. Nigeria.

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INTRODUCTION

Water is one of the most common substances known and a natural resource which is needed for survival. Although spring water is a good source of drinking water, it has relatively little suspended contaminants like dust and bacteria and a significant amount of mineral salts. Since well water can also be used for drinking, it is important to locate it away from subterranean water pollution sources such covered pit latrines with brick lining [1, 2].

The water requirement of man ranges from drinking and personal hygiene to fisheries, agriculture-irrigation, navigation for transport of goods, industrial production, cooling in fossil fuels, power plants, hydro-electric power generation and recreational activities-going to beaches, swimming pools etc.

There are undesirable effects on aquatic environment, examples of these includes urbanization, deforestation, accidental and uncontrolled use and release of chemicals, discharge of untreated waste, leaching from solid waste deposits and uncontrolled/excessive use of fertilizers and pesticides [3, 4, 5, 6]. Activities of these result in waster pollution.

The sign of water pollution is obviously seen to most casual observer. Drinking water tastes bad, mosses or aquatic weeds grow unchecked on many water bodies, ocean, beaches, river and lakes emitting disgusting odours. The diversity of this signs and effects indicate the complexities of the problem [7, 8]. There are various sources of pollutants in the aquatic ecosystem. These include things that aren't thought to be harmful. Many of them add a disagreeable taste and or odor to the water, others significantly upset the ecosystem without beings directly harmful to humans [9, 10].

Other groups however, have direct and indirect influences on the human organism and can cause great damage. Nature has provided no way to get rid of them. Some heavy metals and other substance are common components of natural waters. Although some are essential for living organisms, yet they may become toxic when present in high concentrations [11, 12, 13, 14].

Consumption of water with excess total dissolved solids (TDS) has laxative effects and problems relating to immune system on humans [15]. This calls for attention and in depth study. Egereonu et al [16] and Ike et al [17] made their input in pollution of river water and its analysis using various analytical methods.

MATERIALS AND METHODS

Study Area

River Benue is in Benue state of Nigeria and lies on latitude $7^{o}33^{1}00^{11}N – 7^{o}\ 57^{1}00^{11}N$ and longitude $8^{o}21^{1}00^{11}E – 8^{o}\ 39^{1}00^{11}E$ and is the chief tributary of River Niger of length 1400 km.

The study is centered on River Benue in Makurdi metropolis and the effects of pollution on the quality of water. To ensure that the water is safe and does not transmit organism capable of causing human diseases or chemicals hazardous to human health, the physico-chemical analyses of water samples from ten (10) different locations were carried out. Samples were taken from different places where pollution is endemic, and they were examined for a number of different factors.

Sample Collection

Plastics were used as sample bottles. The bottles were washed with clean brush and detergents, rinsed properly and soaked with about 14% Nitric acid (HNO_3) and left over –night. The average depth and cross-sectional area of the 1.194 km wide river are 7.82 m and 4608.42 m^2, respectively.

The river is full of activities, as fishermen sail on the river looking for their daily bread. Engine boats convey goods and people through the river. At the shore of the river are markets for sale of the fishes and other river creatures. There are also establishments like abattoir and timber factory, which could introduce pollutants into the river.

Ten distinct locations along the Benue River in Makurdi Town provided water samples that were gathered for examination.

The seven samples were taken from the following sources:-

Sample A Benue Brewery Limited

Sample B Benue state university
Sample C Benue links limited
Sample D Makurdi abattoir
Sample E Wurukum
Sample F Makurdi water works
Sample G Wadata
Sample F Igbo
Sample I Naka road
Sample J Agutu

Water sample were taken at distances along the river A,B,C,D,E,F,G,H,I,J

Samples were collected with polyethylene material and stored in refrigerator for analysis. The maximum duration for which the samples are expected to be stored depending on the analyte as given by [18] is given in the Table 1. This means that the analysis for each analyte was done before the specified length of time for storage got expired. Recommended storage condition for some Analytes in water samples (all samples were stored in refrigerator).

Table 1. For water quality analysis, most samples need no preservatives, except nitrates and heavy metals, which are stabilized with H_2SO_4 or HNO_3.

Analyte	**Bottle**	**Preservative**
Alkalinity	p	None
Calcium	p	None
Chloride	p	None
Conductivity	p	None
Hardness	p	None
Magnesium	p	None
Nitrate	p	H_2SO_4
pH	p	None
phosphate	p	None
potassium	p	None
Sodium	p	None
Sulfate	p	None
TSS	p	None
Pb, Fe, Zn, Cu, Cd	p	HNO_3 to pH≤ 2

P=polyethylene Source: Radojeyic et al.

Here Figure 1 shows the River benue for water quality analysis with nitrites and heavy metals

Figure 1. River Benue.

Analysis

Determination of Temperature

After the sample was collected, the measurement was made immediately, and to guarantee perfect equilibrium, the thermometer was submerged in the water sample-containing can for five minutes. With a standard range of 0–100°C, the mercury-in-glass thermometer was calibrated in degrees Celsius.

Determination of pH

Procedure: The pH of the water sample was determined using Consort Digital pH meter. Buffer standards at pH4, pH7, and pH9 were used to calibrate or standardize the pH meter. Following the calibration, soft tissue paper was used to clean the electrode and it was rinsed with distilled water.

Then, the pH of water samples were determined by immersing the glass electrode into water sample and taking the reading.

Determination of Total Hardness

Procedure: Using EDTA as the titrant and Erichrome black-T as the indicator, the titrimetric method was used to determine this [19].

Calculation: Hardness (EDTA) as mg/$CaCO_3$ = A× B× 1000 ml of sample
Where A = ml titration of sample, B = mg $CaCO_3$ equivalent to 1.00 ml EDTA titrant litre.

Determination of Total Suspended Solid

This was done by evaporation method.

Total solid was calculated in milligrams per liter as follows.

$$\text{Total solids as mg/l} = \frac{(W_1 - W_2)\text{g}\,(1000\ \text{mg/g})(1000\ \text{ml/l})}{\text{Sample volume (ml)}}$$

W_1 = Weight of dried residue + dish, W_2 = Weight of empty dish.

Determination Total Dissolved Solids (TDS)

Procedure: HM Digital TDS meter 4 was used to calculate the total dissolved solid. To accomplish this, the TDS meter probe was dipped into the water sample, and the reading was taken straight from the readout.

Determination of Electrical Conductivity

Procedure: The HANNA EC 215 conductivity meter was the electrical conductivity meter that was utilized. A 0.01 KCl solution was used to calibrate the conductivity meter. Deionized water was used to rinse the conductivity meter probe. After that, the probe was dipped into each water sample individually to get the corresponding conductivity reading in µs/cm from the digital readout.

Determination of Total Alkalinity

Procedure: A 250 cm^3 conical flask was pipetted with 25 cm^3 of the sample, and two drops of methyl orange indicator were added. 0.1M HCl acid was added to the solution to titrate it until the color turned orange instead of yellow. The total alkalinity of the water samples is determined using the standard expression below, based on the titre values that were recorded:

$$\text{Alkalinity (mg/l)} = \frac{\text{Titrate value}\times\ \text{Molarity}\times\ 100\times\ 1000}{2\times\ \text{Vol of sample}}$$

Determination of Chemical Oxygen Demand

This was done using Dichromate Reflux Method. Ferrous ammonium sulphate solution Fe $(NH_4)_2SO_4$ titrant and 0.25N potassium dichromate ($K_2Cr_2O_7$) with 4 to 5 drops of Ferrion indicator.

Determination of Biochemical Oxygen Demand

Incubation method was used in the dark to avoid photosynthetic Bacterial degradation for five (5) days was carried out and repeated.

Determination of Dissolved Oxygen

This was determined using HANNA HI 83200 TEST kit.

Determination of Chloride

Using potassium chromate indicator and silver nitrate as a titrant, Mohr's technique was used to determine this [20].

Determination of Nitrate and Sulpate

These were determined by UV spectrophotometer of model DR 2000 using the Hatch corporation method. Nitrate using the nitraver 5 nitrate while Sulphate was determined using sulfaver 4 sulphate, [21, 22, 23].

Determination of Phosphate

This was determined by phosphate 5 phosphate using the Hatch Corporation Method [24]. After about 10 minutes, the absorbance of the blank, standards, and samples were measured at the wavelength of 470 nm, using Nova spectrophotometer of 4049 model. Phosphate concentration of the samples was determined by extrapolation.

Determination of Calcium Hardness

Using EDTA as a titrant and solochrome Blank-T as an indicator, the titrimetric technique was used to determine this [24].

Calculation

$$\text{Calcium hardness as mg } CaCO_3/\text{I} = \frac{\text{A} \times \text{B} \times 1000}{\text{ml Sample}}$$

Where, A = ml titrant for the sample, and B = mg $CaCO_3$, which, at the calcium indicator end point, is equal to 1.00 ml EDTA titrant.

Determination of Sodium

Working Sodium solution containing 2, 4, 6, 10 ppm of Na and 10, 20, 30, 40 ppm of K were prepared. The intensities of emission of blank, standard solutions and samples were then obtained using the Gallene Kamp flame analyzer flame photometer at a specific wavelength of 589 nm for sodium by spraying the sample into the flame. The calibration curve was plotted and the concentrations of sodium and potassium were determined by extrapolation.

Determination of Heavy Metals (Cd, Fe, Cu, Pb, Zn)

The metallic ions Cd, Fe, Cu, Pb and Zn were detected using the atomic absorption spectrophotometer Unican solar 969 model. The metals were detected as reported by Technical Bulletin [25] Tables (2,3,4).

Table 2. Average concentration of physic–chemical parameters determined in River Benue during dry season.

S/N	Parameters	A	B	C	D	E	F	G	H	I	J	Mean	WHO
1	Temperature ^oC	26.2	26.80	27.30	27.40	28.0	27.20	27.50	26.9	27.6	27.1	27.2	25.0-30.0
2	pH	6.10	6.50	5.90	7.05	6.80	6.35	6.0	6.40	6.55	6.84	6.39	6.5-8.5
3	Total Hardness(mg/L)	18.0	20.5	25.1	20.1	22.3	23.1	19.4	24.2	23.7	26.5	21.2	500
4	TSS(mg/L)	52.0	37.0	102.4	140.5	89.8	180.0	64.4	68.5	72.6	48.6	95.2	500

S/N	Parameters	A	B	C	D	E	F	G	H	I	J	Mean	WHO
5	TDS(mg/L|)	24.5	29.3	49.6	21.4	38.2	27.8	34.5	34.2	30.7	32.8	32.2	1000
6	EC(μ)	39.6	54.3	49.9	62.1	40.5	80.5	69.4	40.9	54.2	50.4	56.5	1250
7	Alkalinity(mg/L)	18.8	20.6	30.0	34.2	26.2	32.8	24.6	26.7	25.4	22.8	26.7	100
8	COD(mg/L)	80.0	70.9	140.0	110.2	120.0	96.4	42.4	52.8	64.2	72.6	94.3	40
9	BOD(mg/L)	20.1	24.6	27.5	18.9	34.8	25.4	30.20	23.4	22.9	28.7	25.9	10
10	DO(mg/L)	3.50	4.68	2.82	3.24	4.25	3.34	3.60	3.84	4.00	3.90	3.63	9.20
11	Chloride(mg/L)	16.8	15.88	18.6	21.55	16.2	22.8	19.85	22.6	18.8	20.4	18.9	250
12	Nitrate(mg/L)	1.24	2.4	3.2	3.8	2.6	4.2	3.0	2.2	2.4	2.8	21.9	45
13	Phosphate(mg/L	0.64	0.40	1.15	0.50	0.45	1.35	0.57	0.80	1.20	0.73	0.65	5.0
14	Sulphate(mg/L)	11.46	14.10	8.90	6.30	16.4	10.2	7.8	10.7	12.4	8.6	10.7	200
15	Calcium(mg/L)	1.5519	1.231	1.0655	1.623	2.0527	1.324	1.824	1.530	2.032	1.422	1.53	75
16	Sodium (mg/L)	3.054	2.169	2.860	3.342	2.652	2.613	2.980	2.240	3.025	2.81	2.81	200
17	Cadmium(mg/L)	0.004	0.011	0.005	0.001	0.002	0.001	0.002	0.004	0.006	0.003	0.002	10
18	Iron(mg/L)	0.022	0.028	0.0428	0.0320	0.026	0.034	0.035	0.024	0.018	0.028	0.0314	0.03
19	Copper(mg/L)	1.0549	1.0751	2.0337	1.1704	1.1127	1.0735	1.6900	1.034	1.120	1.042	1.316	1.0
20	Lead(mg/L)	0.213	ND	0.268	0.195	0.124	ND	ND	ND	0.008	0.012	0.116	0.05
21	Zinc(mg/L)	0.562	0.834	1.084	1.282	1.190	1.861	0.986	1.024	0.638	0.760	1.114	5.0

Table 3. Average concentration of physico–chemical parameters determined in River Benue during rainy season.

S/N	Parameters	A	B	C	D	E	F	G	H	I	J	MEAN
1	Temperature ° C	25.4	26.4	26.8	26.0	26.8	27.3	28.0	25.8	27.4	27.0	26.69
2	Ph	6.15	6.00	6.87	6.85	5.98	6.67	6.57	6.05	6.03	6.89	6.41
3	Total hardness(mg/L)	45.2	40.1	47.6	34.8	41.3	38.0	39.8	42.4	45.0	44.5	41.87
4	TSS (mg/L)	38.0	42.0	80.0	120.4	69.6	78.0	56.2	57.8	68.0	70.0	68.0
5	TDS (mg/L)	80.0	72.4	94.6	76.0	83.0	85.4	78.0	68.2	60.2	62.4	76.02
6	EC (μS/cm)	54.3	60.2	117.9	80.5	90.0	94.4	100.2	108.0	110.0	98.0	91.35
7	Alkalinity (mg/L)	20.0	26.0	40.6	34.0	29.8	32.4	48.0	50.2	46.4	47.0	37.44
8	COD (mg/L)	80.0	106.4	120.0	160.4	100.0	140.3	130.0	98.6	106.0	102.0	114.37
9	BOD (mg/L)	20.1	24.2	30.5	40.0	27.5	25.4	20.0	22.4	19.0	19.6	24.87
10	DO (mg/L)	2.06	2.00	4.68	3.70	2.82	4.25	3.34	3.22	2.96	2.80	3.18
11	Chloride (mg/L)	20.4	24.0	32.0	28.2	44.0	35.4	33.2	19.8	24.0	22.8	28.38
12	Nitrate (mg/L)	2.8	2.4	3.2	2.6	2.0	3.4	2.9	4.2	2.2	3.2	2.89
13	Phosphate (mg/L)	0.64	0.62	0.50	0.81	1.2	0.87	0.45	0.82	1.0	0.76	0.85
14	Sulphate (mg/L)	20.8	22.1	18.4	23.5	30.5	36.1	32.0	42.4	38.0	32.6	29.64
15	Calcium (mg/L)	1.65	1.24	1.068	1.84	3.24	2.82	2.64	2.20	2.19	1.84	2.07
16	Sodium (mg/L)	2.84	2.60	3.20	4.00	4.80	2.90	1.84	2.20	2.40	2.70	2.95
17	Cadmium (mg/L)	0.006	0.008	0.012	0.018	0.024	0.010	0.013	0.009	0.005	0.008	0.011
18	Iron (mg/L)	0.01	0.03	0.41	0.291	0.42	0.02	0.025	0.035	0.001	0.001	0.124
19	Copper (mg/L)	0.98	1.024	0.84	0.90	1.03	1.12	1.08	1.04	0.92	0.80	0.9734
20	Lead (mg/L)	<0.001	ND	<0.01	0.011	0.012	0.001	0.001	ND	ND	0.001	0.00281
21	Zinc (mg/L)	0.58	0.628	0.94	1.24	2.8	2.14	2.04	2.0	1.94	1.86	1.6168

Table 4. Physico–chemical parameters determined in River Benue during rainy season and dry season.

S/No	Dry X	Rainy Y	XY	X^2	Y^2
1	27.2	26.69	725.968	739.84	712.3561
2	6.45	6.41	41.3445	41.6025	41.0881

S/No	Dry X	Rainy Y	XY	X^2	Y^2
3	22.28	41.87	932.8636	496.3984	1753.0969
4	85.61	68	5821.48	7329.0721	4624
5	32.31	76.02	2425.2062	1043.9361	5779.0404
6	54.1	91.35	4942.035	2926.81	8344.8225
7	26.18	37.44	980.1792	685.3924	1401.7536
8	84.97	114.37	9718.0189	7219.9009	13080.499
9	25.63	24.87	637.4181	656.8969	618.5169
10	3.72	3.18	11.8296	13.8384	10.1124
11	19.41	28.38	550.8558	376.7481	805.4244
12	2.78	2.89	8.0342	7.7284	8.3521
13	0.73	0.85	0.6205	0.5329	0.7225
14	10.66	29.64	315.9624	113.6356	878.5296
15	1.57	2.07	3.2499	2.4649	4.2849
16	2.78	2.95	8.201	7.7284	8.7025
17	0.007	0.011	0.000077	0.000049	0.000121
18	0.029	0.124	0.003596	0.000841	0.015376
19	1.24	0.9734	1.207016	1.5376	0.947508
20	0.00865	0.00281	0.00002431	0.00007482	0.000007896
21	1.021	1.6168	1.65075	1.04244	2.61404
	∑X 408.68565	∑Y 559.70801	∑XY 27,157.12836	$\sum X^2$ 21,665.107	$\sum Y^2$ 38,074.87685

RESULTS AND DISCUSSION

Using Pearsons Product Moment correlation Coefficient;

$$r = \frac{n\sum XY - \sum X \sum Y}{\sqrt{(n\sum X\ 2 - (\sum X\ 2)(n\sum Y\ 2 - (\sum Y)2}}$$

n = 21

$\sum XY$ = 27,157.12836

$(\sum X)$ = 408.68565 $(\sum X)^2$ = 167,023.9605

$(\sum Y)$ = 559.70801 $(\sum Y)^2$ =313,273.0565

$\sum X^2$ =21,665.107

$\sum Y^2$ =38,074.87685

$$r = \frac{(21(27,157.12836) - ((408.68565)(559.70801)}{\sqrt{(21(21,665.107) - 167023.9605)(21(38,074.87685) - 313,273.0565}}$$

$$r = \frac{570,299.6956 - 288,744.6319}{\sqrt{(287,943.2865)(486,299.3574)}}$$

$$r = \frac{341,555.0637}{\sqrt{(1.400266352 \times 10\ 11)}}$$

r = 341,555.0637

374,201.3298

= 0.912757482

= 0.91

The value or r = 0.91 shows that there is excellent positive correlation between the parameters studied in both dry and rainy seasons.

Here Table 5 shows the water quality with different parameters

Table 5. The table shows water quality parameters, with temperature, pH, and total hardness within acceptable limits, but COD, BOD, copper, and lead exceeding WHO standards.

S/N	Parameters	Minimum	Maximum	Mean(ci)	Standard Deviation	WHO(Lij)	Mean/WHO Ci/Lij
1	Temperature	26.2	28.0	27.2	0.53	25.0-30.0	0.984
2	pH	5.90	7.05	6.39	0.39	6.5-8.5	0.852
3	Total hardness(mg/L)	18.0	25.10	21.2	2.24	500	0.042
4	TSS (mg/L)	37.0	180.0	95.2	44.2	500	0.190
5	TDS (mg/L)	21.4	49.9	32.2	8.85	1000	0.032
6	EC (µS/cm)	39.6	80.5	56.5	13.46	1250	0.045
7	Alkalinity (mg/L)	18.8	32.8	26.7	5.43	100	0.267
8	COD (mg/L)	42.4	14.0	94.3	30.36	40	2.36
9	BOD (mg/L)	18.9	34.8	25.9	5.14	10	2.59
10	DO (mg/L)	2.82	4.25	3.63	0.59	9.20	0.395
11	Chloride (mg/L)	15.9	22.8	18.9	2.51	250	0.076
12	Nitrate (mg/L)	10.6	38.2	21.9	8.43	45	0.487
13	Phosphate (mg/L)	0.40	1.35	0.65	0.36	5.0	0.13
14	Sulphate (mg/L)	6.30	16.4	10.7	3.24	200	0.054
15	Calcium (mg/L)	1.0655	2.0527	1.53	0.32	75	0.02
16	Sodium (mg/L)	2.169	3.342	2.81	0.35	200	0.014
17	Cadmium (mg/L)	0.001	0.005	0.002	0.0037	10	0.0002
18	Iron (mg/L)	0.022	0.0428	0.0314	0.0061	0.03	1.047
19	Copper (mg/L)	1.0549	2.0337	1.316	0.22	1.0	1.316
20	Lead (mg/L)	0.0038	0.213	0.116	0.38	0.05	2.32
21	Zinc (mg/L)	0.562	1.861	1.114	0.38	5.0	

Results with ANN

Matlab application was utilized for the analytical plots presented (ANOVA determination) and ANN model was deployed to predict the outcome of the physico-chemical parameters obtained. The ANOVA outcome was generated with 'anova2' command that generated the anova table figure, the box and whisckers plot and the multi-comparative outcome that stated the significant difference between the dry and rainy season data obtained.

The ANN had one input data which was the positions of the physico-chemical parameters and one target data leading to the output which was the mean of the samples obtained. Five hidden neurons were utilized and the data analytics carried in the ANN were 70% of the data for training, 15% of the data a piece were utilized for testing and validation process and the training algorithm utilized was the Levenberg macquart back propagation network Figures 2–11.

RESULTS OF THE ACTUAL DATA OBTAINED

ANN Predictions

ACTUAL And ANN Predicted Comparative Analysis

Results of The Physiochemical Parameters

Analysis of variance of the physio-chemical parameters

Temperature

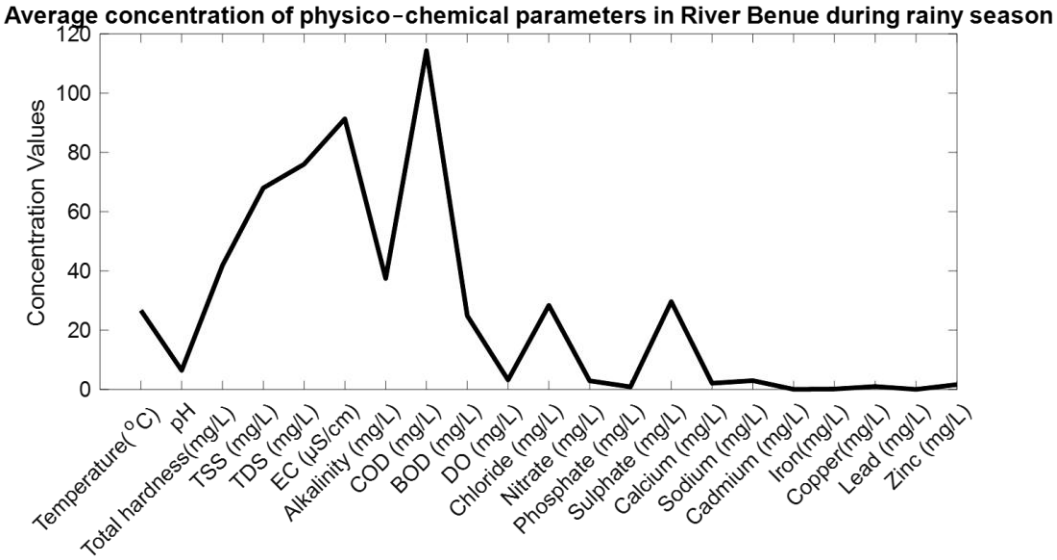


Figure 2. Average Concentration of Physico-Chemical Parameters in River Benue during Rainy Season.

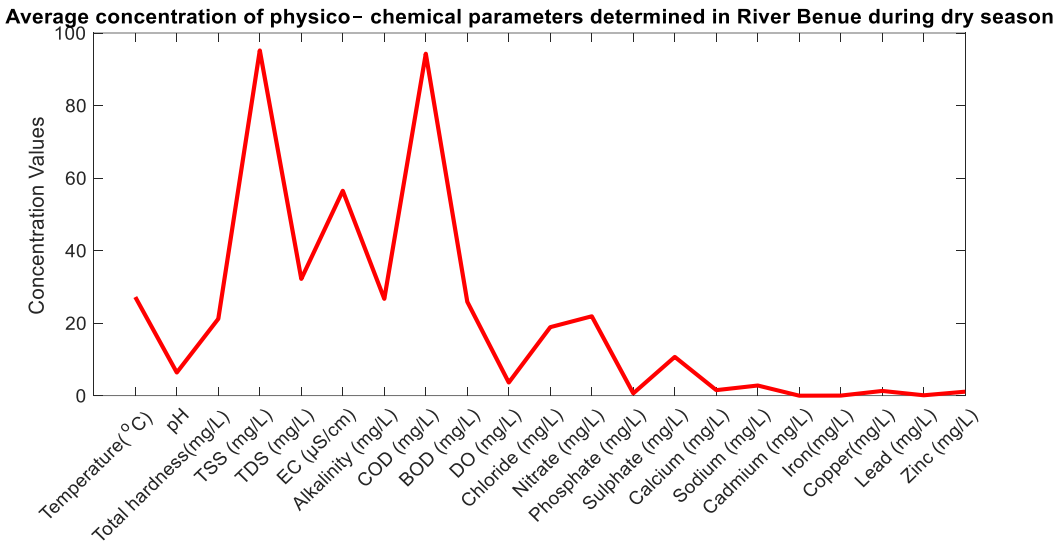


Figure 3. Average Concentration of Physico-Chemical Parameters in River Benue during Dry Season.

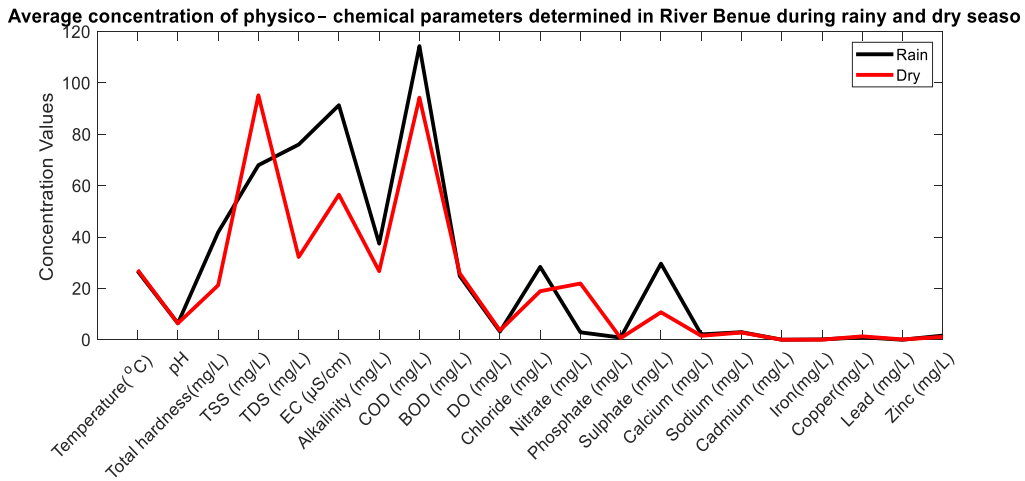


Figure 4. Comparative Analysis of Physio-Chemicals obtained during dry and Rainy season.

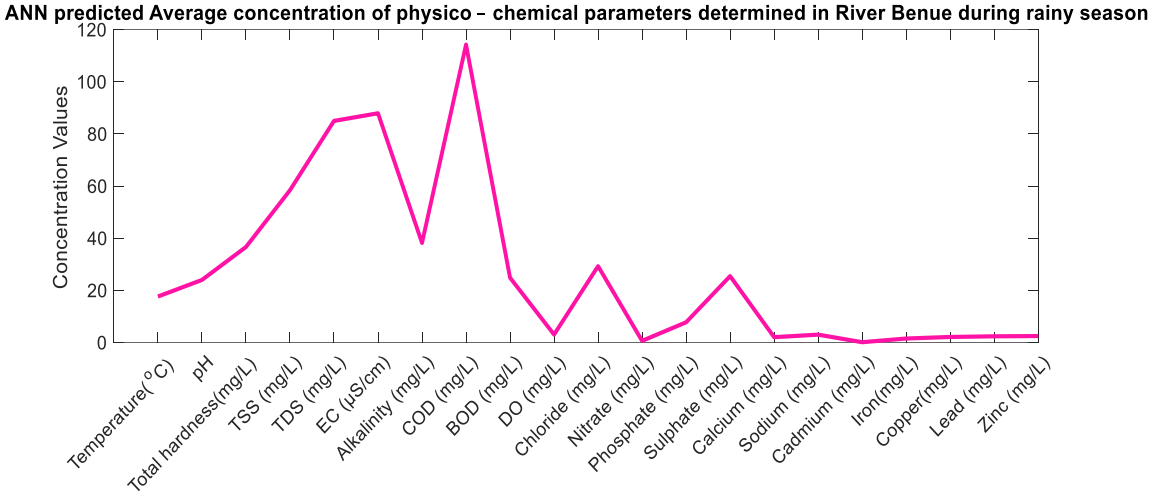


Figure 5. ANN Predicted Average physio-chemical parameters for Rainy.

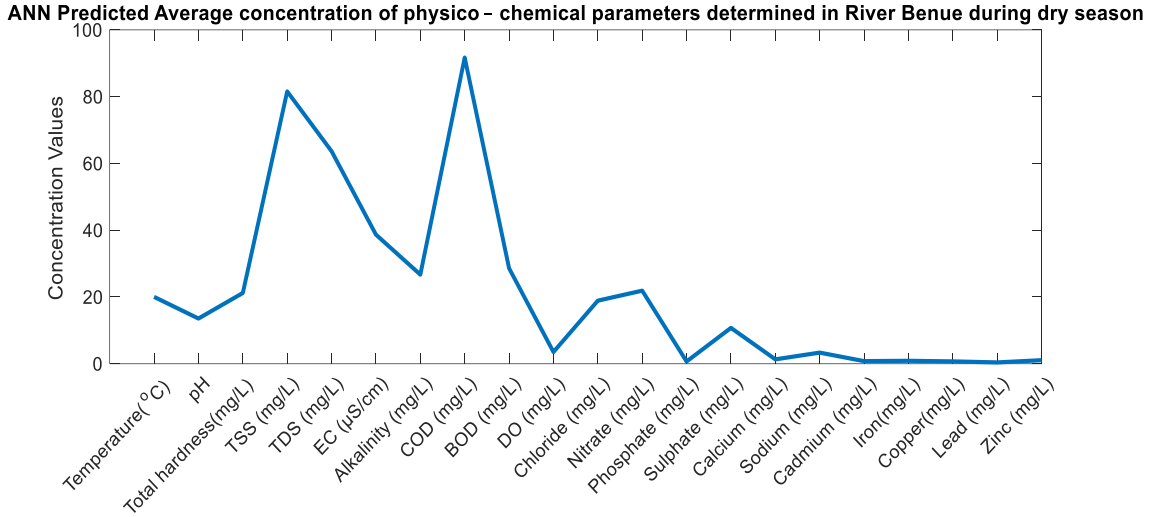


Figure 6. ANN Predicted Average physio-chemical parameters for Dry.

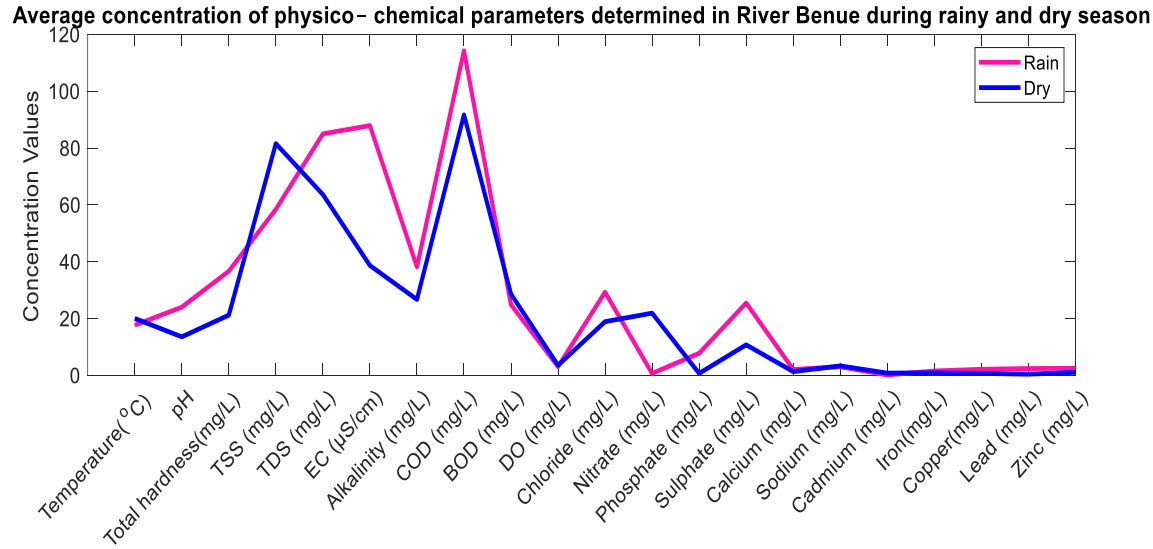


Figure 7. ANN Comparative Analysis of Physico-Chemicals obtained during dry and Rainy season.

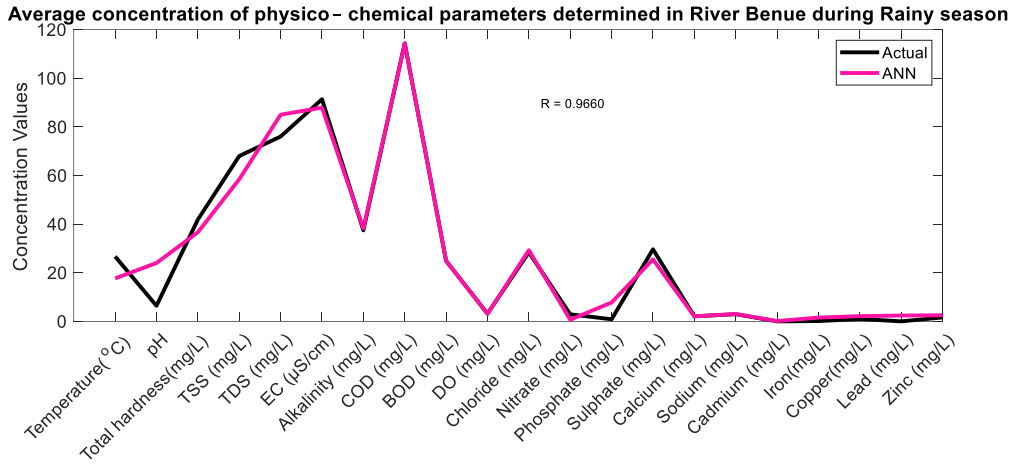


Figure 8. Comparative analysis of the actual parameters and ANN predicted parameters with R value of 0.9660 for rainy season.

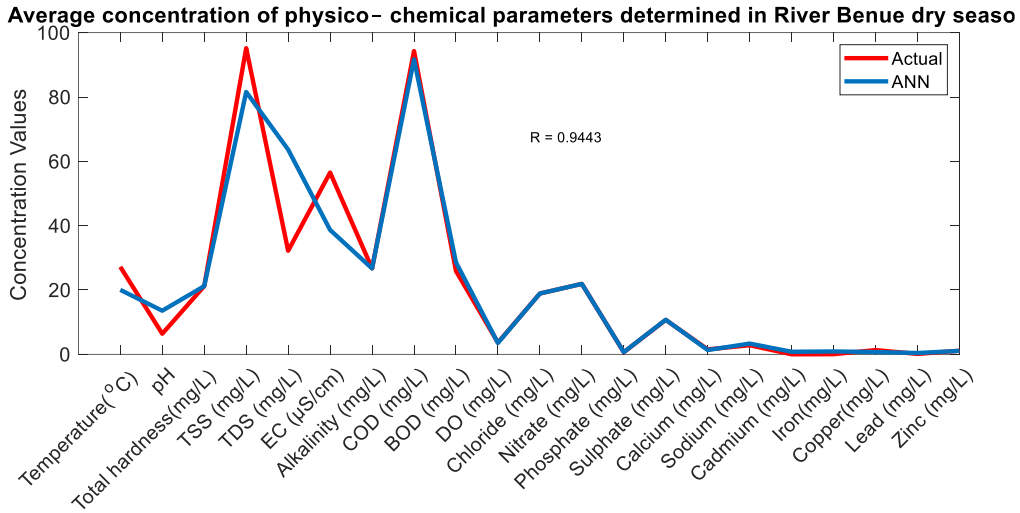


Figure 9. Comparative analysis of the actual parameters and ANN predicted parameters with R value of 0.9443 for the dry season.

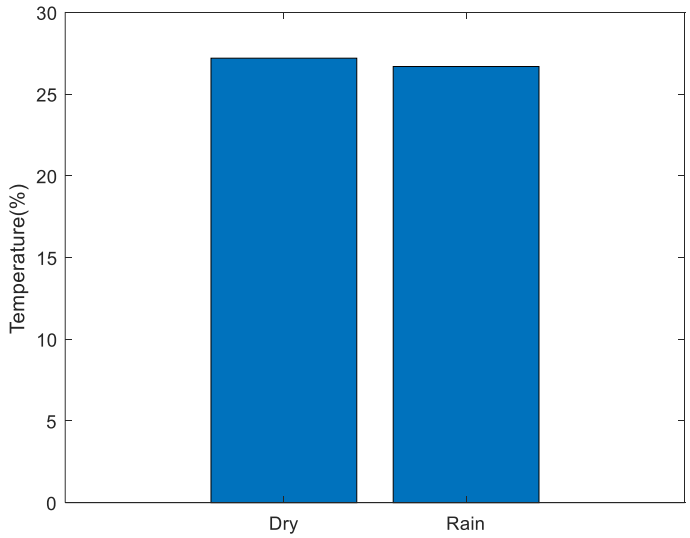


Figure 10. Comparative analysis data of temperature between the dry and rainy season temperature.

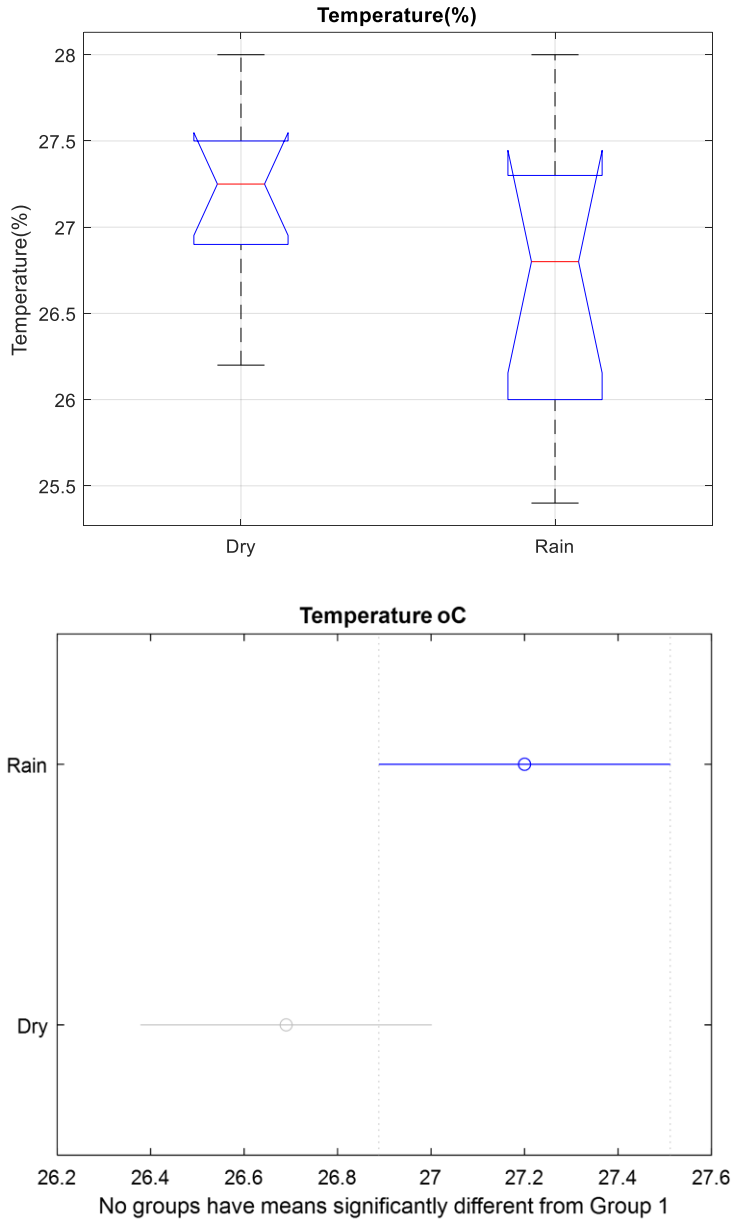


Figure 11. Box and Whiscker's plot.

Here Table 6 shows the Multi-comparative plot for temperature for different parameters

Table 6. Multi-comparative plot.

ANOVA Table

Source	SS	df	MS	F	Prob>F
Columns	1.3005	1	1.3005	2.95	0.1029
Error	7.929	18	0.4405		
Total	9.2295	19			

Here the Table 7–24 and Figures 12–30 are showing the water quality analysis with using different kind of parameters (heavy metals and nitrites) such as pH, hardness, TSS, EC, Alkalinity, COD, BOD, DO, Chloride, Nitrate, Phosphate, Sulphates, Calcium, Sodium, Iron, Copper, Lead, Zinc

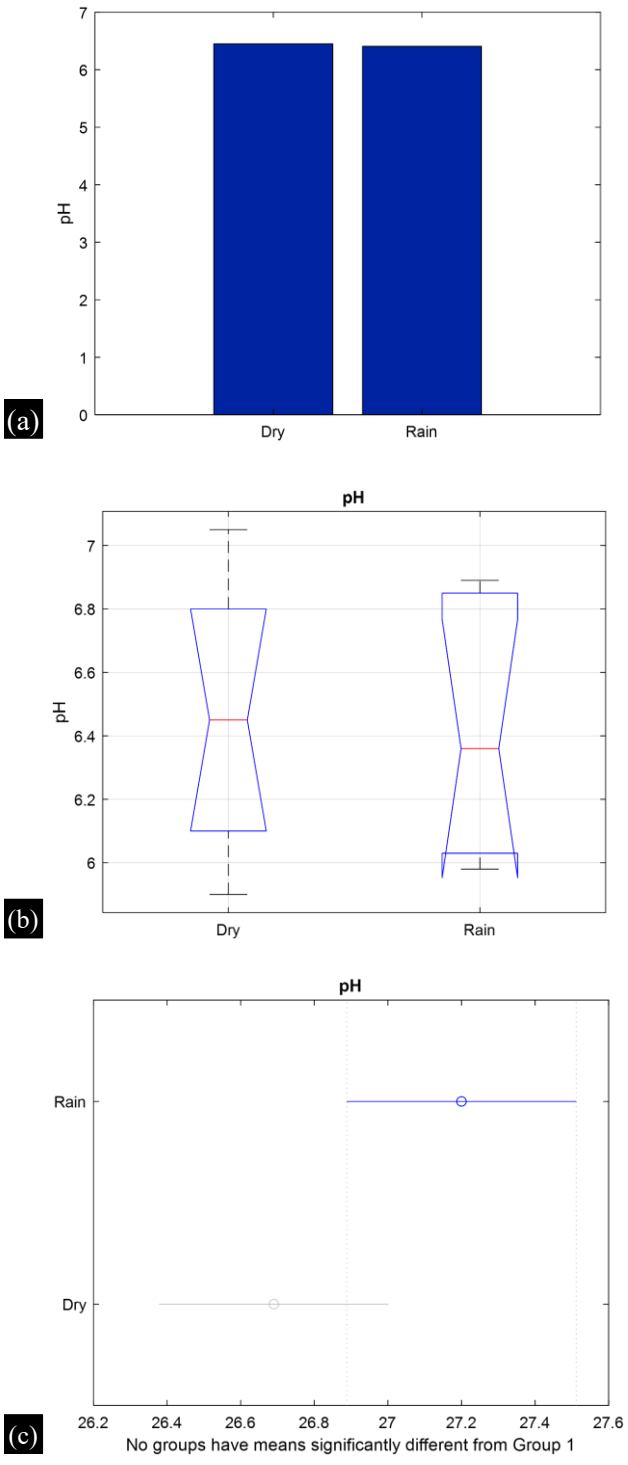
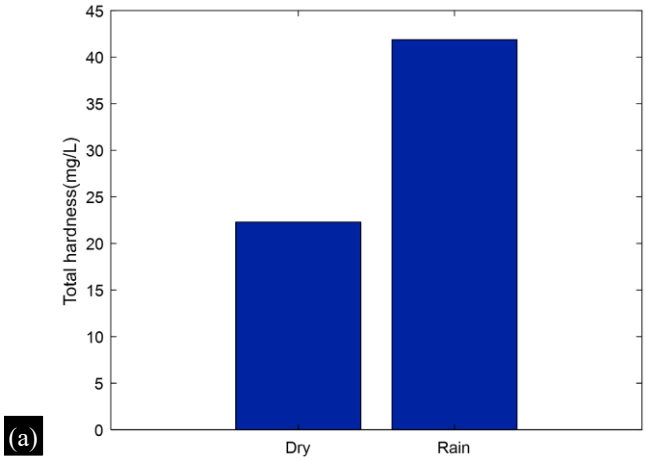


Figure 12. pH.

Table 7. ANOVA table for pH.

ANOVA Table

Source	SS	df	MS	F	Prob>F
Columns	0.00924	1	0.00924	0.06	0.8071
Error	2.71033	18	0.15057		
Total	2.71957	19			



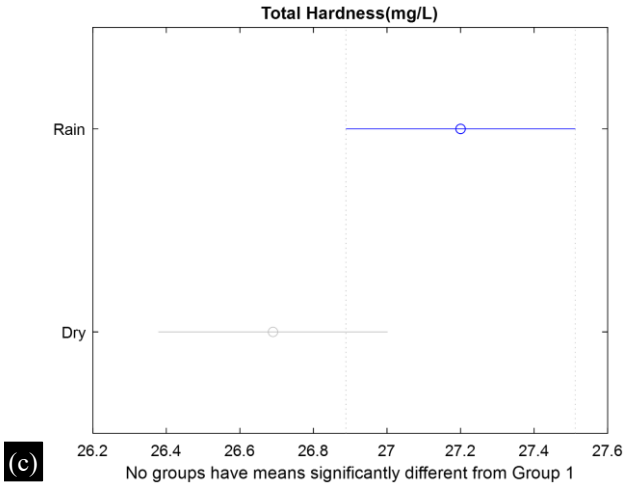


Figure 13. Total hardness(mg/L).

Table 8. ANOVA table for total hardness.

ANOVA Table

Source	SS	df	MS	F	Prob>F
Columns	1916.88	1	1916.88	172.27	1.1769e-10
Error	200.29	18	11.13		
Total	2117.17	19			

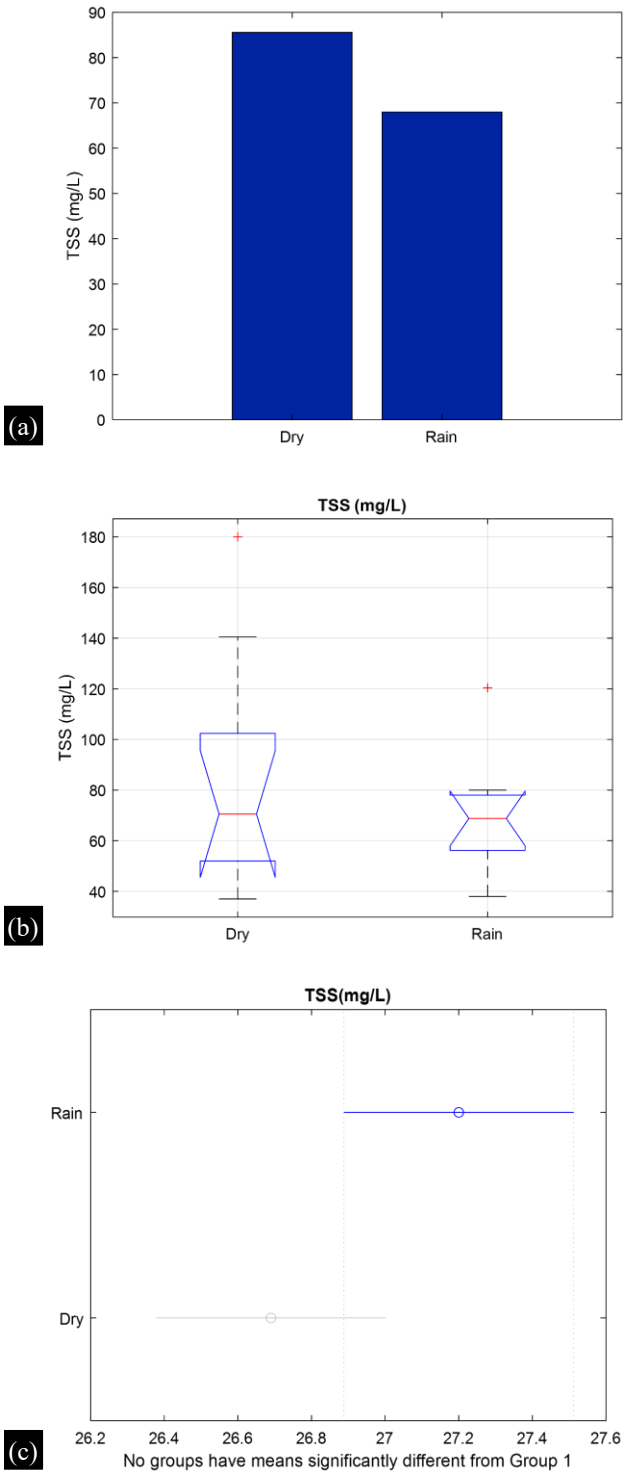
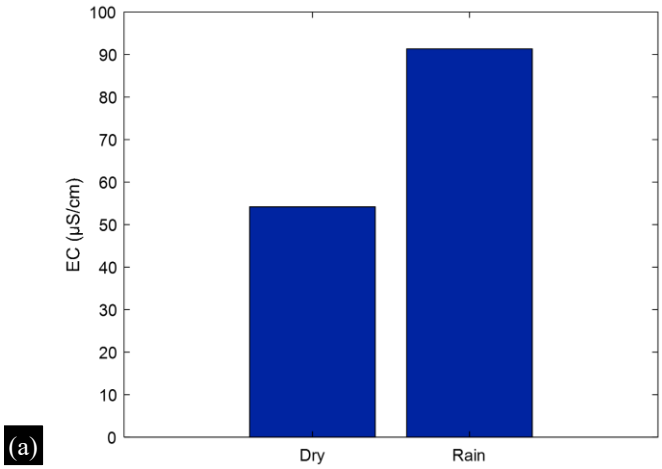


Figure 14. TSS in (mg/L).

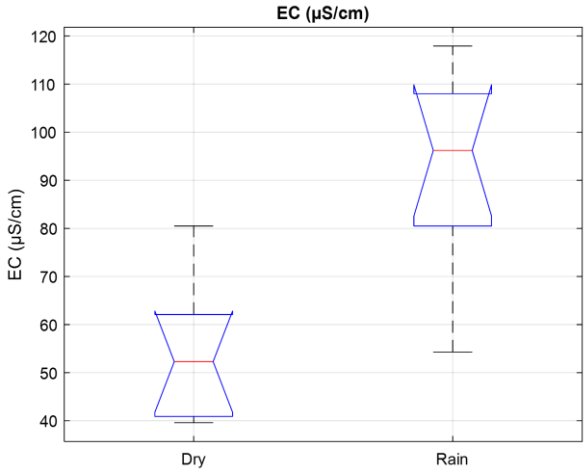
Table 9. ANOVA table for TSS (mg/L).

ANOVA Table

Source	SS	df	MS	F	Prob>F
Columns	1545.3	1	1545.28	1.22	0.284
Error	22811.6	18	1267.31		
Total	24356.9	19			



(a)



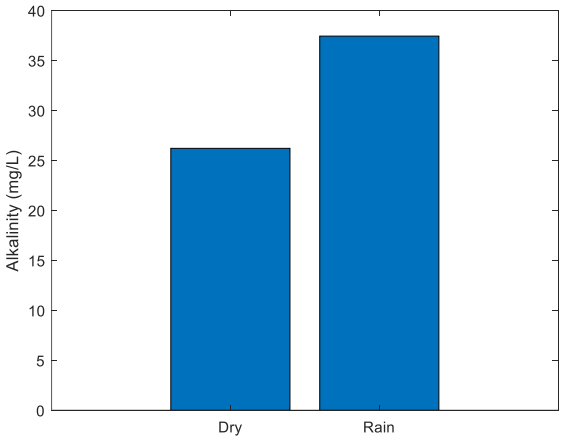
(b)

Figure 15. EC(µS/cm^{-1}) for dry and rainy season.

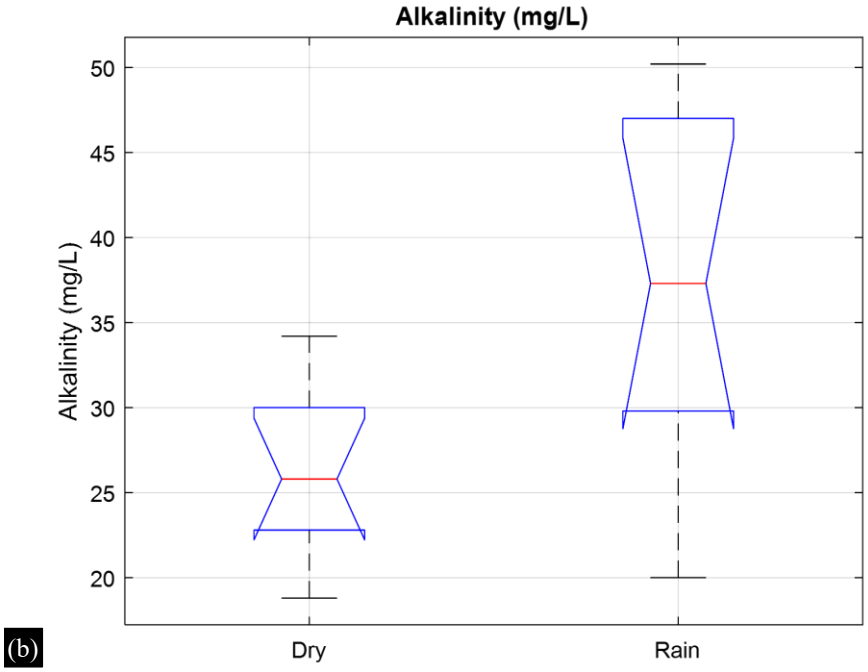
Table 10. ANOVA table for EC(µS/cm^{-1}).

ANOVA Table

Source	SS	df	MS	F	Prob>F
Columns	6908	1	6908.04	22.53	0.0002
Error	5520.2	18	306.68		
Total	12428.2	19			



(a)



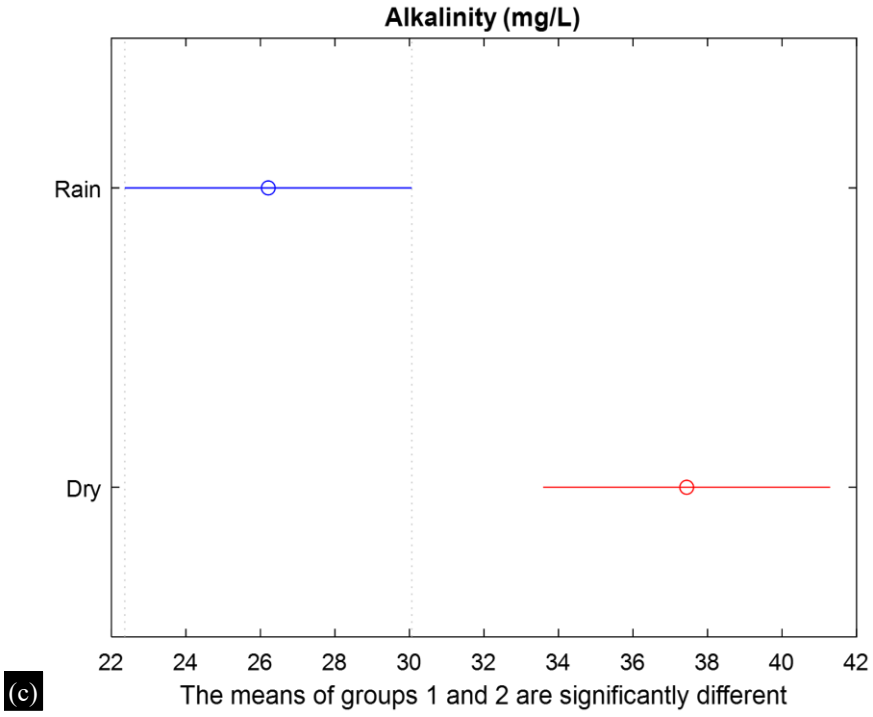
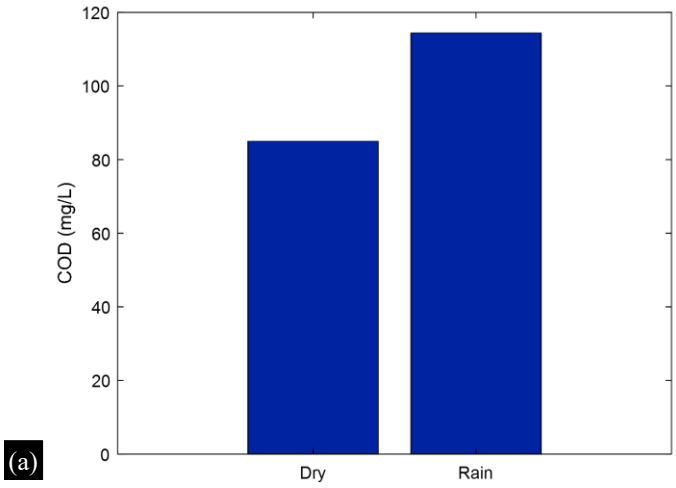


Figure 16. Alkalinity (mg/L) for dry and rainy season.

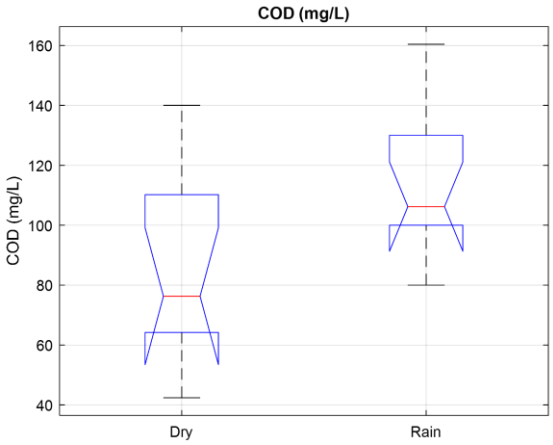
Table 11. ANOVA table for Alkalinity (mg/L) for dry and rainy season.

ANOVA Table

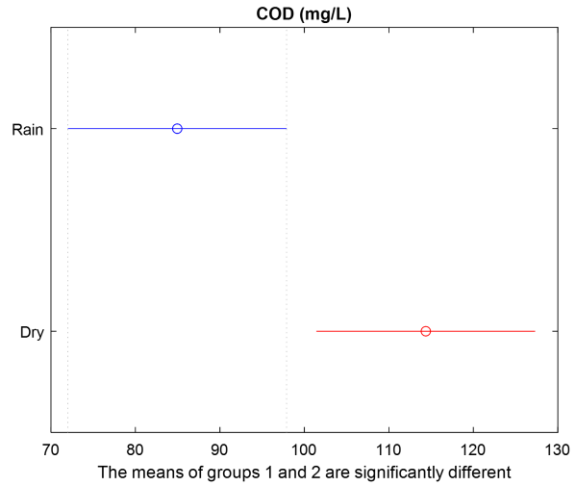
Source	SS	df	MS	F	Prob>F
Columns	630.56	1	630.564	9.38	0.0067
Error	1209.75	18	67.209		
Total	1840.32	19			



(a)



(b)



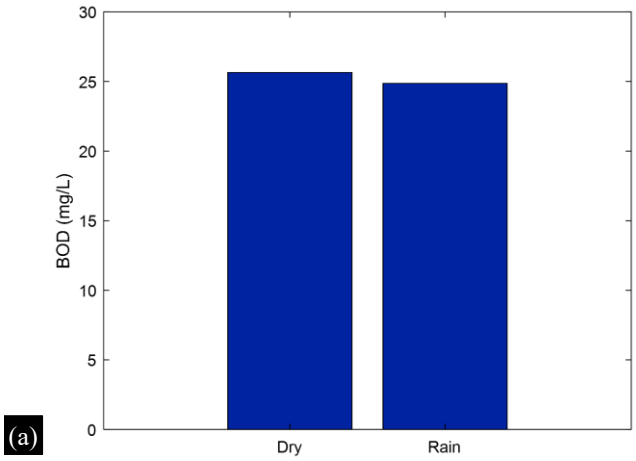
(c)

Figure 17. COD (mg/L) for dry and rainy season.

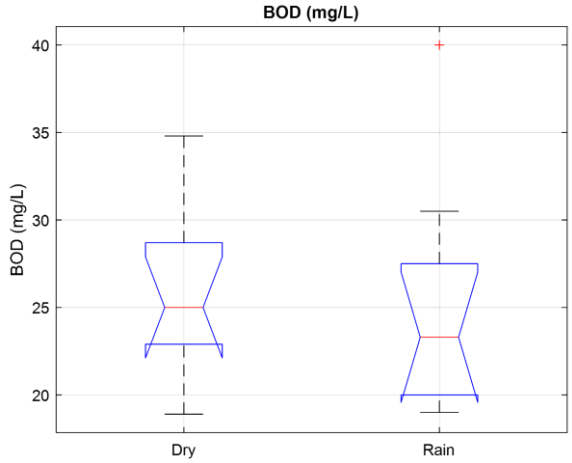
Table 12. ANOVA table for COD (mg/L) for dry and rainy season.

ANOVA Table

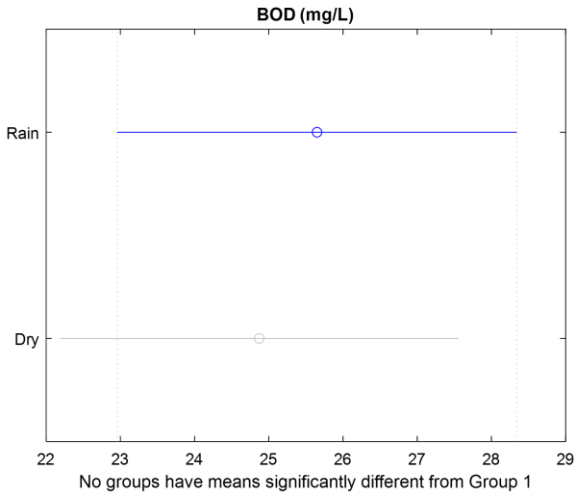
Source	SS	df	MS	F	Prob>F
Columns	4327.7	1	4327.68	5.7	0.0281
Error	13667	18	759.28		
Total	17994.7	19			



(a)



(b)



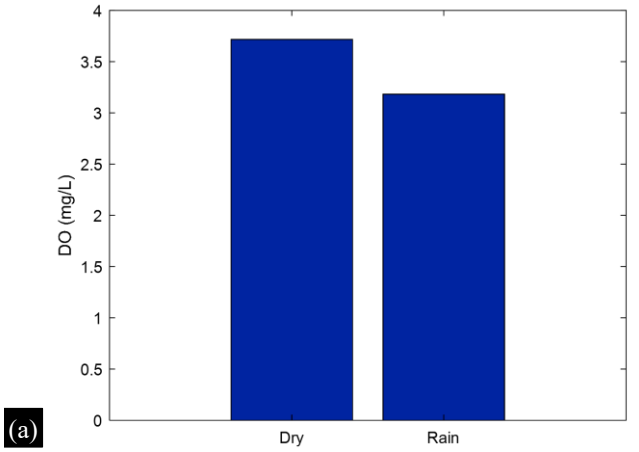
(c)

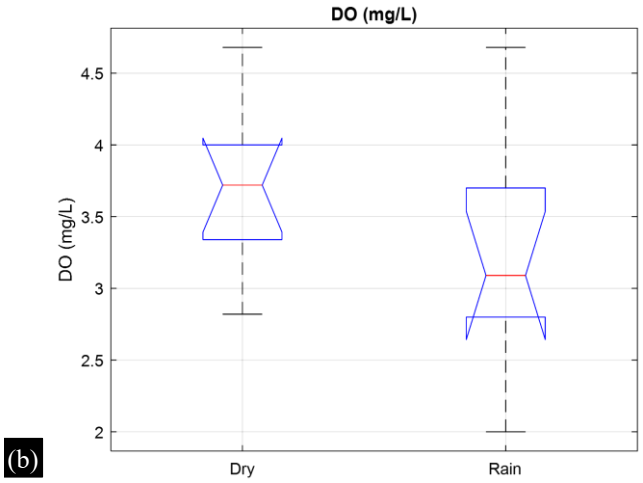
Figure 18. BOD (mg/L) for dry and rainy season.

Table 13. BOD (mg/L) for dry and rainy season.

ANOVA Table

Source	SS	df	MS	F	Prob>F
Columns	3.042	1	3.042	0.09	0.7642
Error	590.366	18	32.7981		
Total	593.408	19			





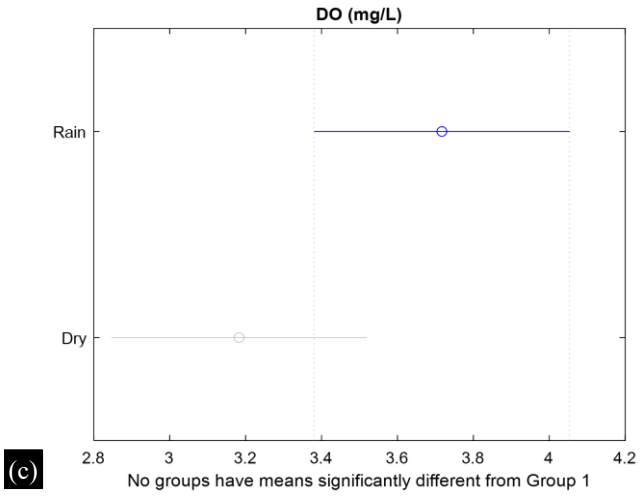
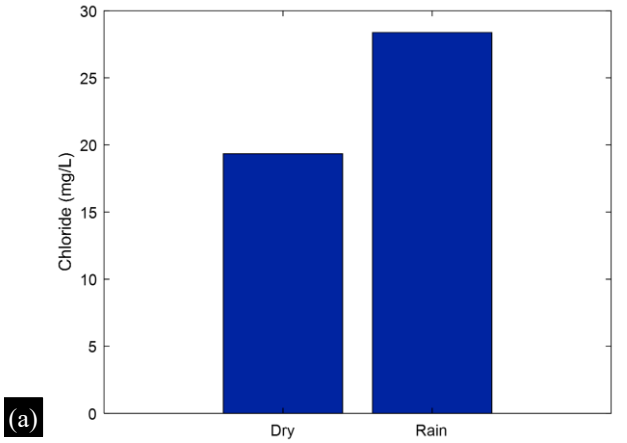


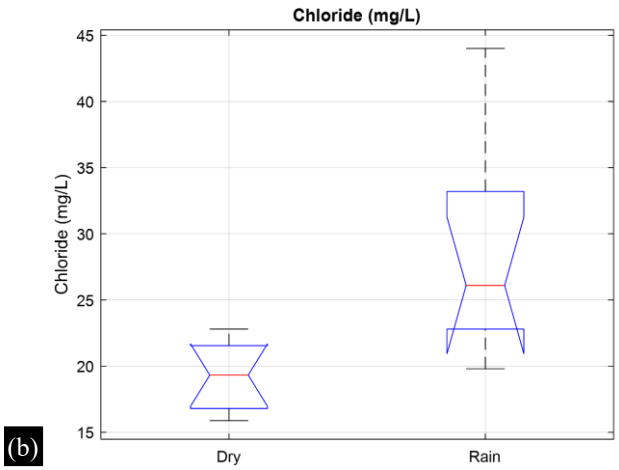
Figure 19. DO(mg/L) for dry and rainy season.

Table 14. ANOVA table for dry and rainy season.

ANOVA Table

Source	SS	df	MS	F	Prob>F
Columns	1.4258	1	1.42578	2.78	0.1128
Error	9.2368	18	0.51316		
Total	10.6626	19			





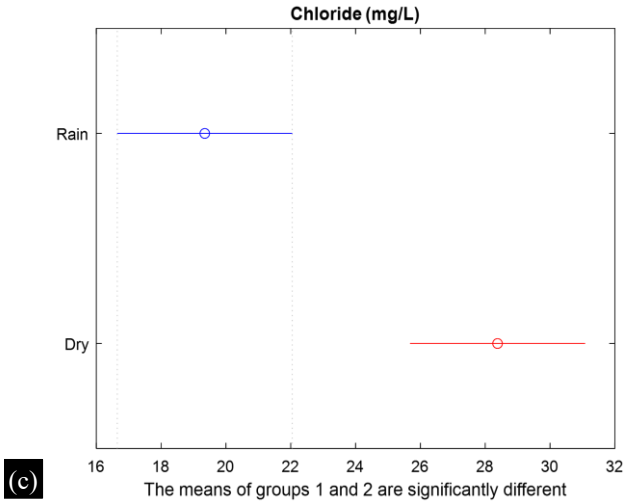


Figure 20. Chloride (mg/L) for dry and rainy season.

Table 15. ANOVA table for dry and rainy season.

ANOVA Table

Source	SS	df	MS	F	Prob>F
Columns	407.89	1	407.885	12.35	0.0025
Error	594.42	18	33.024		
Total	1002.31	19			

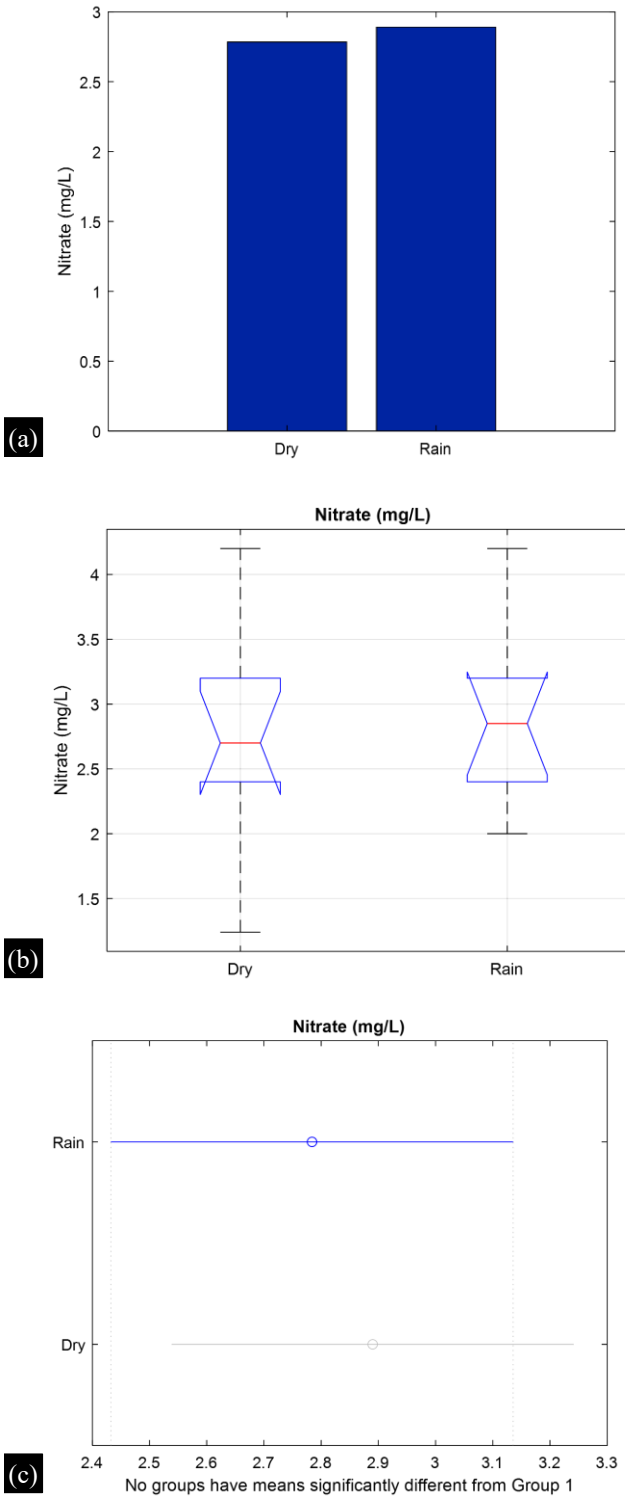


Figure 21. Nitrate (mg/L) for dry and rainy season.

Table 16. ANOVA table for Nitrate (mg/L) for dry and rainy season.

ANOVA Table

Source	SS	df	MS	F	Prob>F
Columns	0.0562	1	0.05618	0.1	0.7551
Error	10.08	18	0.56		
Total	10.1362	19			

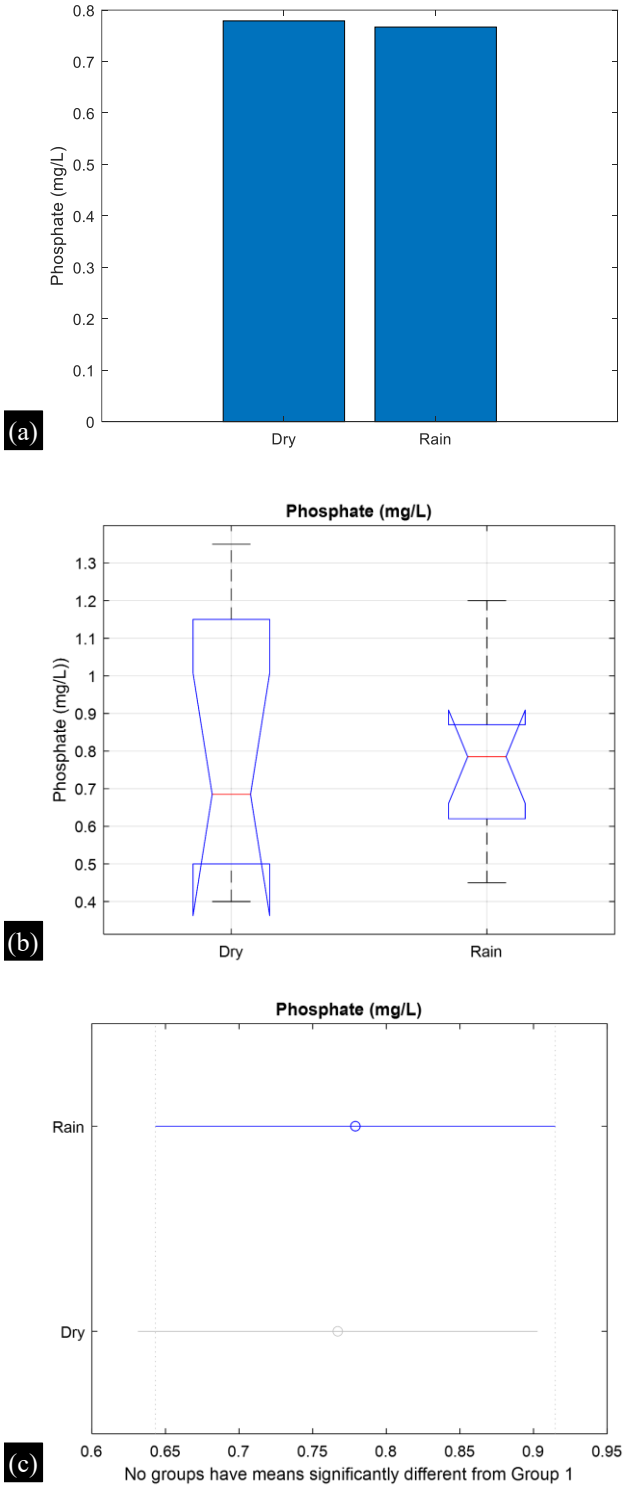
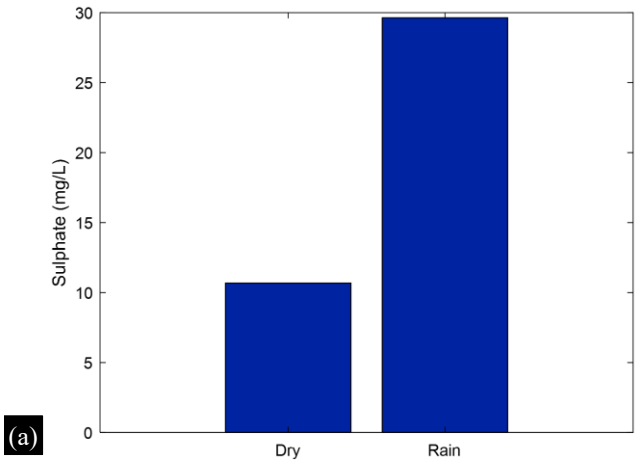


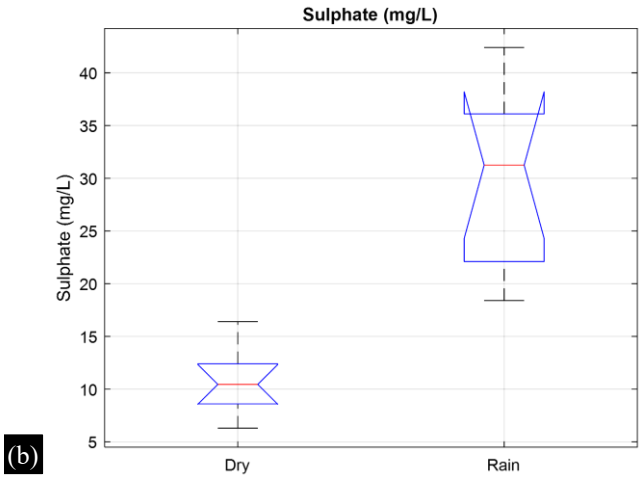
Figure 22. Phosphate (mg/L) for dry and rainy season.

Taable 17. ANOVA table for Phosphate (mg/L) for dry and rainy season.

ANOVA Table

Source	SS	df	MS	F	Prob>F
Columns	0.00072	1	0.00072	0.01	0.927
Error	1.5031	18	0.08351		
Total	1.50382	19			





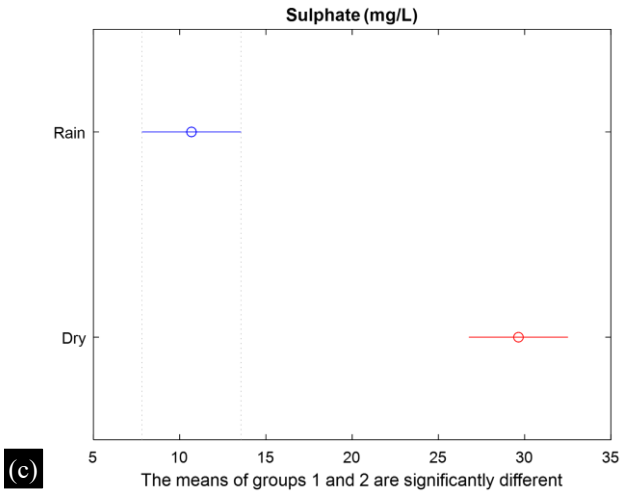
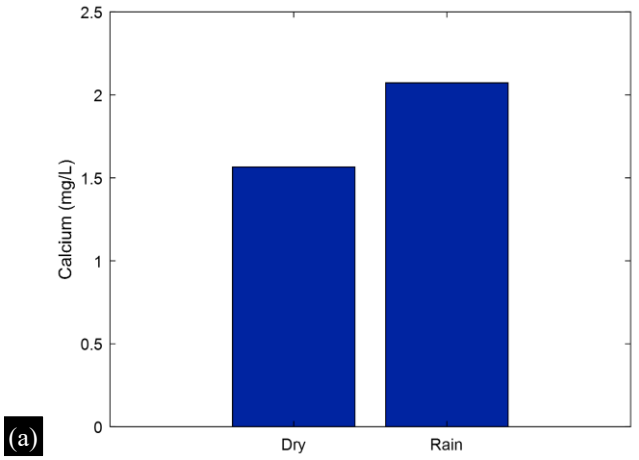


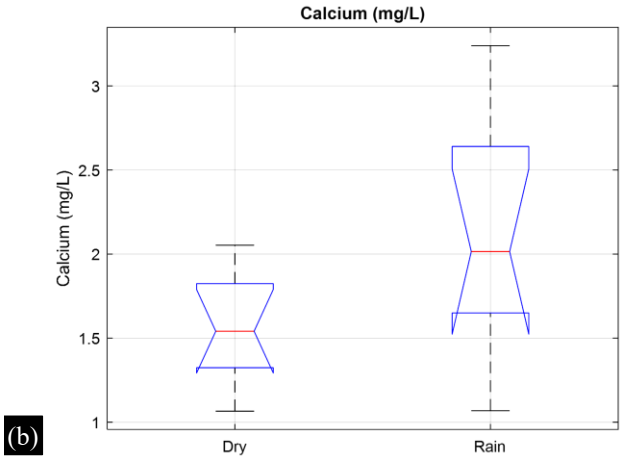
Figure23. Sulphate (mg/L) for dry and rainy season.

Table 18. ANOVA table for Sulphate (mg/L) for dry and rainy season.

ANOVA Table

Source	SS	df	MS	F	Prob>F
Columns	1796.27	1	1796.27	48.13	1.75025e-06
Error	671.73	18	37.32		
Total	2468	19			





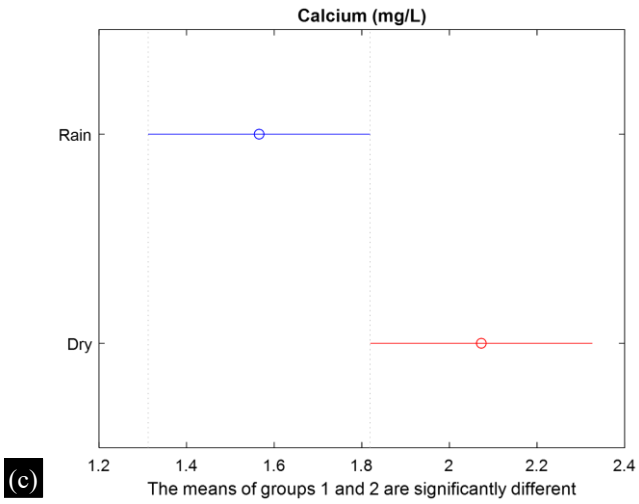


Figure 24. Calcium (mg/L) for dry and rainy season.

Table 19. ANOVA table for Calcium (mg/L) for dry and rainy season.

ANOVA Table

Source	SS	df	MS	F	Prob>F
Columns	1.28621	1	1.28621	4.43	0.0497
Error	5.22999	18	0.29056		
Total	6.5162	19			

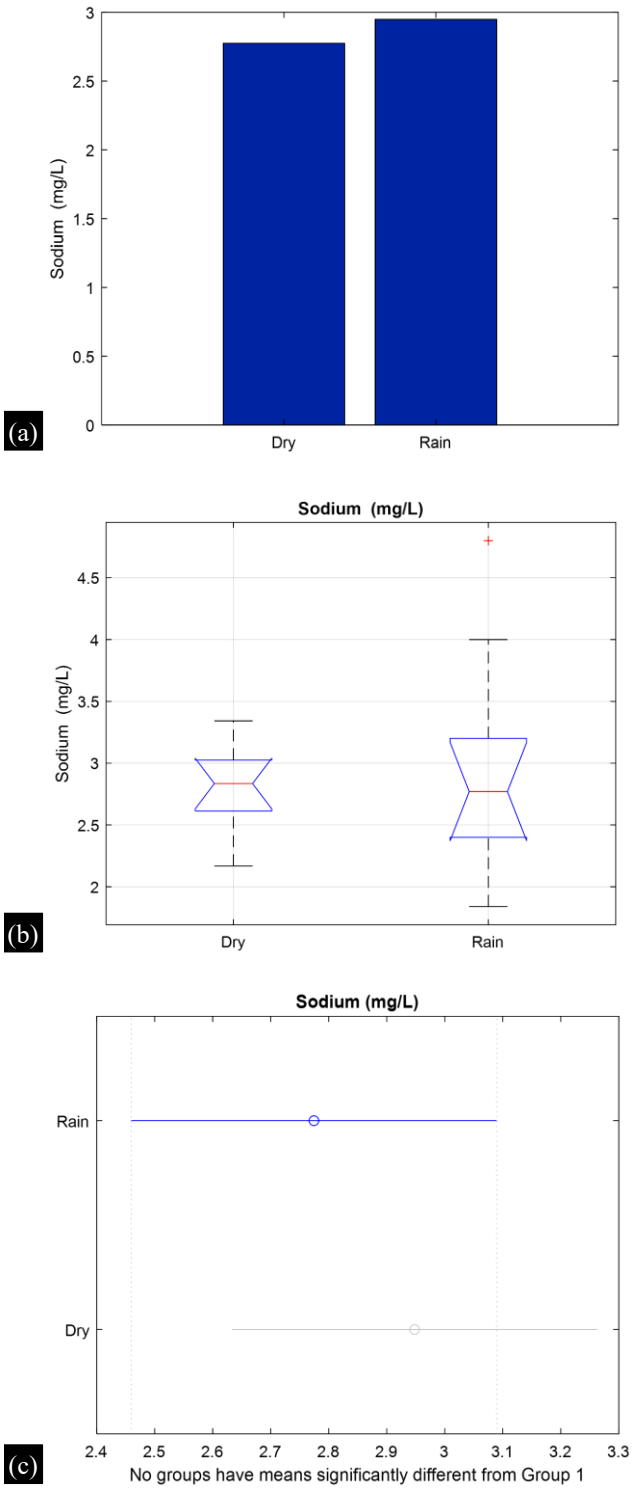
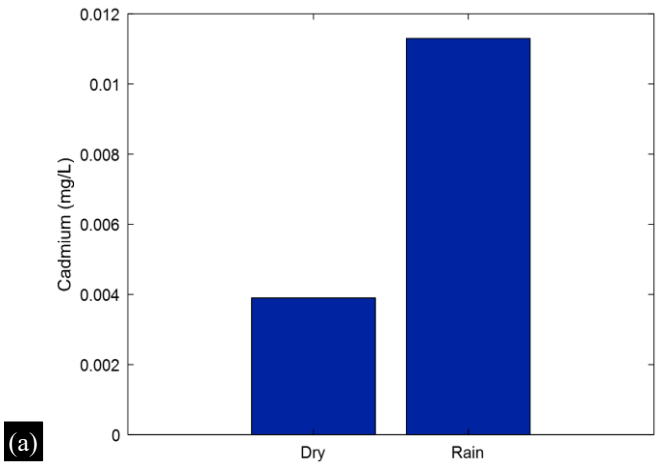


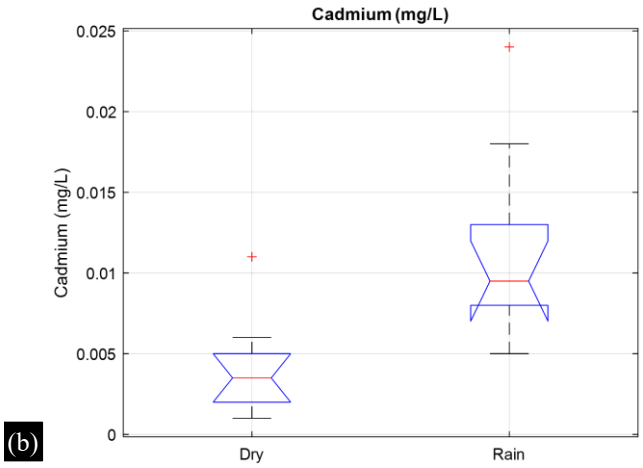
Figure 25. Sodium (mg/L) for dry and rainy season.

Table 20. ANOVA table for Sodium (mg/L) for dry and rainy season.

ANOVA Table

Source	SS	df	MS	F	Prob>F
Columns	0.15051	1	0.15051	0.33	0.57
Error	8.0913	18	0.44952		
Total	8.24181	19			





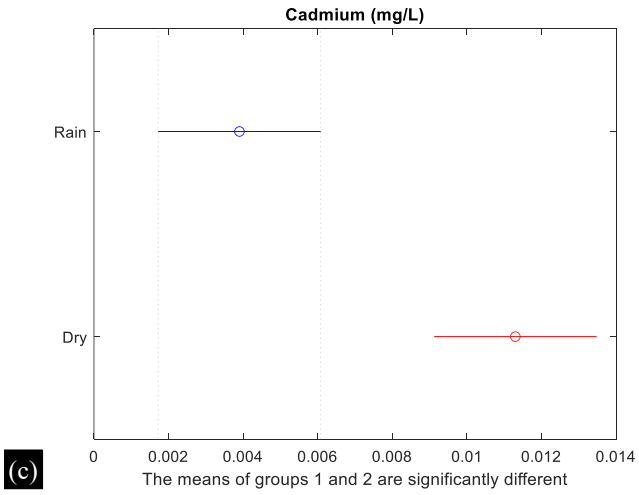


Figure 26. Cadmium (mg/L) for dry and rainy season.

Table 21. ANOVA table for Cadmium (mg/L) for dry and rainy season.

ANOVA Table

Source	SS	df	MS	F	Prob>F
Columns	0.00027	1	0.00027	12.73	0.0022
Error	0.00039	18	0.00002		
Total	0.00066	19			

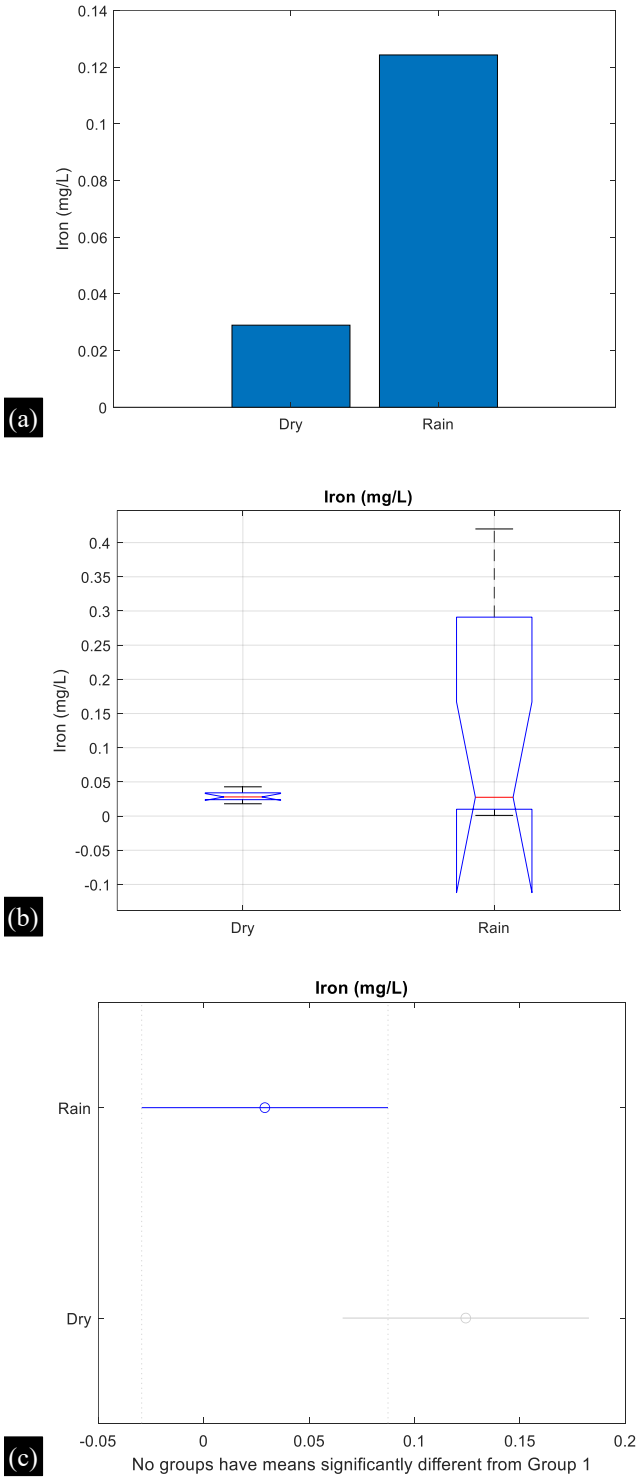
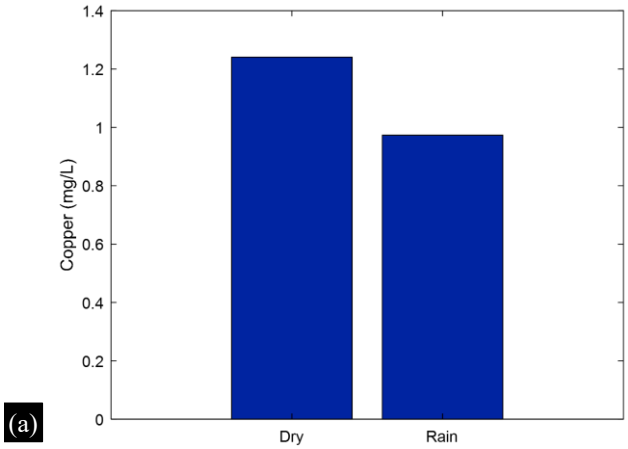


Figure 27. Iron (mg/L) for dry and rainy season.

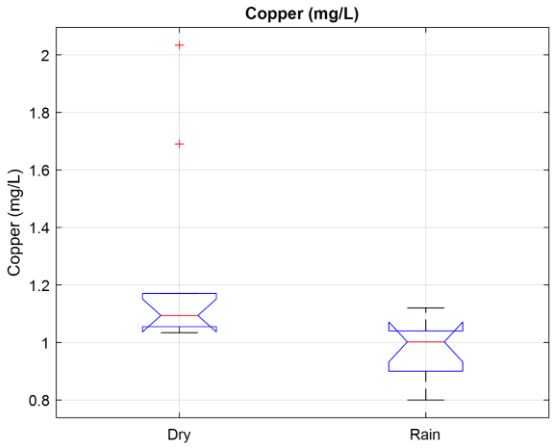
Table 22. ANOVA table for Iron (mg/L) for dry and rainy season.

ANOVA Table

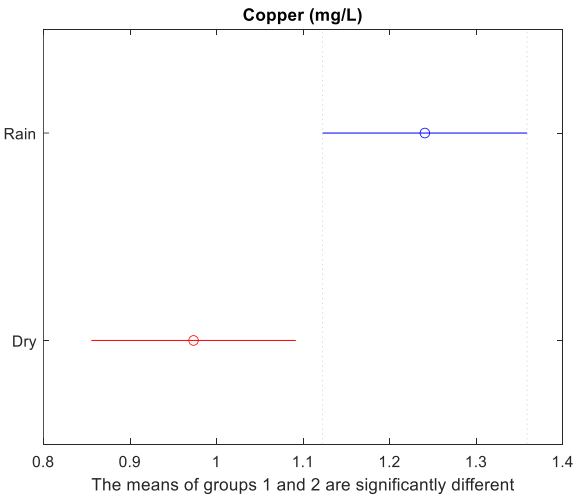
Source	SS	df	MS	F	Prob>F
Columns	0.04543	1	0.04543	2.94	0.1037
Error	0.27839	18	0.01547		
Total	0.32382	19			



(a)



(b)



(c)

Figure 28. Copper (mg/L) for dry and rainy season (a) Copper (mg/L) (b) Copper (mg/L) (b) Copper (mg/L).

Table 23. ANOVA table for Copper (mg/L) for dry and rainy season.

ANOVA Table

Source	SS	df	MS	F	Prob>F
Columns	0.35706	1	0.35706	5.65	0.0288
Error	1.13792	18	0.06322		
Total	1.49498	19			

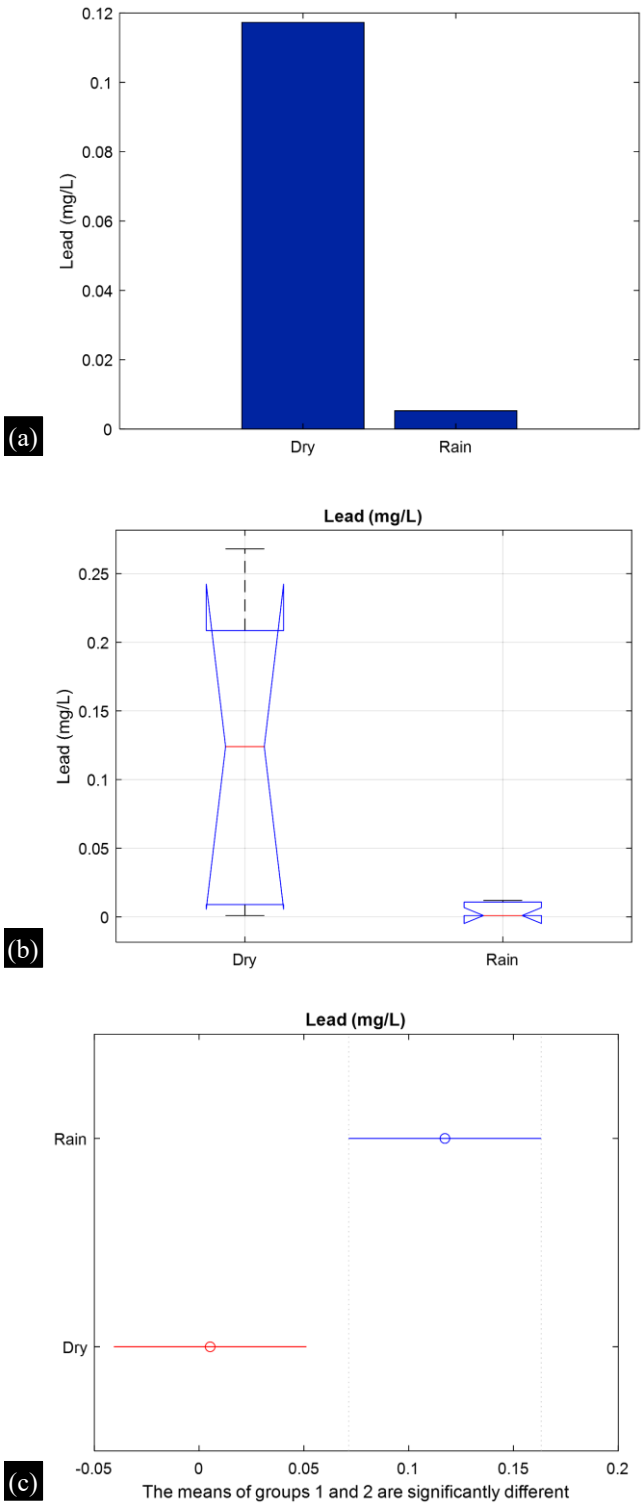


Figure 29. Lead (mg/L) for dry and rainy season.

Table 24. ANOVA table for Lead (mg/L) for dry and rainy season.

ANOVA Table

Source	SS	df	MS	F	Prob>F
Columns	0.0439	1	0.0439	7.05	0.0209
Error	0.07468	12	0.00622		
Total	0.11859	13			

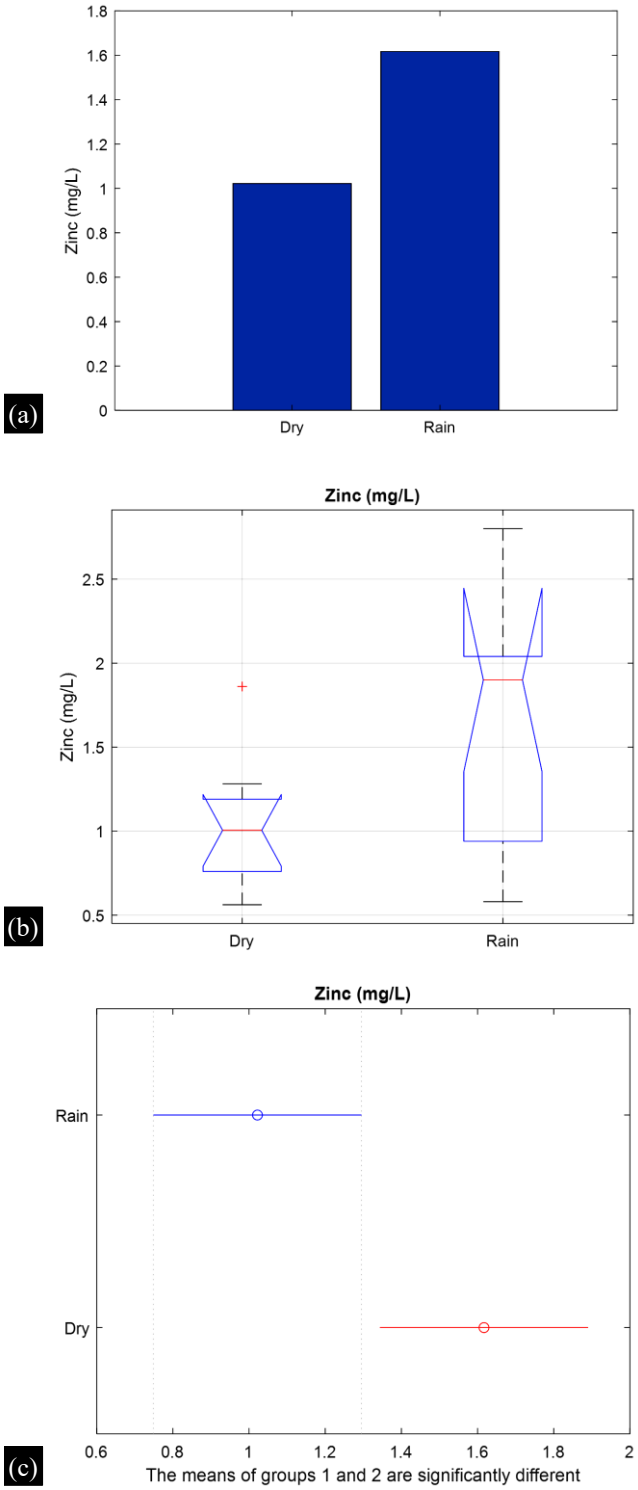


Figure 30. Zinc (mg/L) for dry and rainy season.

Table 25. ANOVA table for Zinc (mg/L) for dry and rainy season.

ANOVA Table

Source	SS	df	MS	F	Prob>F
Columns	1.76834	1	1.76834	5.23	0.0345
Error	6.08389	18	0.33799		
Total	7.85223	19			

DISCUSSION

Temperature: The mean value for dry season is 27.20°C which is higher than 26.69°C for rainy. Even though the values are within the acceptable limit of WHO standard [26], the higher value for dry is obvious due to the intensity of sunshine and the dry environment/atmosphere.

pH: The pH values are 6.45 and 6.41 for dry and rainy seasons respectively. This shows that the water is slightly acidic. The values are within the 6.5-8.5 range of WHO limit for portable water.

Total Hardness: The values for dry and rainy are 22.8 mg/L and 41.87 mg/L respectively. It could be observed that the value for rainy is almost twice that of dry. This could be attributed to washing away of domestic refuse/sewage, topsoil &rocks by flood/erosion during rainy season. The values are far lower than the WHO limit permissible limit of 500 mg/L. It can therefore produce later easily with soap but may lack some essential minerals like $Ca^{2+}$and Mg^{2+} ions needed for proper body functioning.

TSS: The values are 85.61 mg/L and 68.0 mg/L for dry & rainy seasons respectively; the higher values for dry season may be connected to the road transport system involving dusts from vehicles; in addition to the smoke particles from the nearby industries and other nefarious human activities that introduce materials containing particles that could not dissolve in water.

TDS: The mean values of TDS are 32.31 mg/L and 76 mg/L for dry and rainy season respectively. This is in contrast to the TSS above this might be expected since the rainfall in rainy season, in itself contains dissolved particles/compounds like CO_2 in addition to the run offs from agricultural activities, and more dissolution of sewage/refuse at dumpsites. Even though the total solids (TS) sum of the TSS and the TDS 117.92 mg/L and 144.02 mg/L for the dry & rainy respectively are below the 500 mg/L highest desirable level of WHO, it does not make the water potable since other parameters would be considered.

EC: The results show that there was higher electrical conductivity values in rainy season with 91.35 $Smolcm^{-1}$ than the 54.10 $Smolcm^{-1}$ for dry season. It should be noted that EC is a function of the ions present in solution. The observation supports the values obtained in their TDS.

Alkalinity: While 26.18 mg/L was obtained in the dry season, 37.44 mg/L was obtained in the rainy season

COD: The values obtained are 84.97 mg/L and 114.37 mg/L for dry and rainy seasons respectively. The values are more than double of the limit of 40 mg/L for portable water, this is not unconnected with industrial activities of the brewery companies and others run offs from agricultural activities involving fertilizers, in addition to quarries/mines resulting from non-point source.

BOD: The mean values of 25.63 mg/L and 24.87 mg/L were obtained for dry & rainy seasons respectively. This implies that the water contains biodegradable organisms at both seasons. These values are very close indicating approximately equal activities of the biodegradable organisms and the extent of pollution of the water. The values are much higher than the WHO permissible limit of 10 mg/L; indicating that the water is highly polluted.

DO: The mean values of 3.72 mg/L and 3.18 mg/L were obtained for dry and rainy seasons respectively. This is in line with the observed values of COD, TDS and EC. Ca^{2+}, SO_4^{2-}, PO_4^{3-} where the values for rainy season are higher leading to lower concentration of oxygen to be dissolved. This is in contrast to the lower values observed in dry season, hence DO. This implies that the aquatic lives in the river would be in jeopardy of asphyxia more in rainy season.

Anions: (Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^-) All the anions studied are present more in rainy season than in dry

season with values of 19.41 mg/L and 28.38 mg/L for Cl^-;2.78 mg/L and 2.89 mg/L for NO_3^-; 0.73 mg/L and 0.85 mg/L for PO_4^{3-} and 10.66 mg/L and 29.64 mg/L for SO_4^{2-}.In all the lower values are for the dry season while the higher values are for rainy season. This trend manifested clearly in the TDS and EC where the values for the rainy season took the toll. Again, the presence of these acidic radicals more in the rainy season could explain why the water of the river is more acidic in the rainy season with average pH value of 6.41 as against 6.45 of dry season.

The implication is that there would be more cultural eutrophication in the rainy season than in dry season, hence the river would produce foul odour more in the rainy season. In practice, this is observed as testified by the inhabitants of the area of the study.

Metallic ions: The concentrations of Ca^{2+} were 1.57 mg/L and 2.07 mg/L for dry & rainy seasons respectively. While that of Fe are 0.029 mg/L and 0.124 mg/L for dry and rainy seasons. This could further explain the reason for higher total hardness in the rainy season as observed.

The concentration of Na was 2.78 mg/L and 2.95 mg/L, Cu is 1.24 mg/L and 0.09734 mg/L; Zn 1.021 mg/L and 1.616 mg/L for dry and rainy seasons respectively; Even though these elements are required for normal body functioning; they are present in far less concentration than the WHO maximum permissible level of 500 mg/L for Na, 1 mg/L for Cu; and 5.0 mg/L for Zn.

The mean values of 0.00281 mg/L observed in lead in rainy season and 0.00865 mg/L in dry season are below 0.05 mg/L WHO highest desirable level; but this does not make the water suitable for drinking, especially since values for 0.007 mg/L and 0.011 for dry and rainy seasons obtained for Cd exceeded the 0.003 mg/L WHO highest desirable level. Since Pb and Cd are heavy metals and are toxic.

CONCLUSION

The Pearson Product Moment Correlation Coefficient was used to establish a correlation between the mean values of each parameter. With an r-value of 0.91, it is evident that these metrics have a strong positive association during the two seasons under investigation.

This implies that the status of the river as it concerns its portability is the same, irrespective of the little fluctuation that might be observed in the different season. It can be concluded from the result of this study that water quality in River Benue is contaminated and polluted. Therefore, it is unsafe for drinking and other domestic activities. Besides it would not encourage recreational activities like swimming.

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