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A Seasonal Assessment of Groundwater Pollution due to Biochemical Oxygen Demand, Chemical Oxygen Demand and Elevated Temperatures in Enugu Northern Senatorial District, South East Nigeria.

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Abstract: *The Biochemical Oxygen Demand (BOD) of groundwater in Enugu Northern Senatorial District of South-east Nigeria have been found to indicate a general high degree of pollution. The Chemical Oxygen Demand (COD) of the water was also assessed and temperature measured. The parameters were determined using standard methods by the Association of Official Analytical Chemists (AOAC) and the American Public Health Association, American Water Works Association; World Environmental Federation (APHA-AWWA-WEF). 12 boreholes were randomly sampled due to depth and spatial distribution and the parameters determined in triplicates on weekly bases for a period of six months. The results were collated in terms of seasons and statistically analysed using a two-factor Analysis of Variance (ANOVA) followed by a post-hoc test of multiple comparisons at p (0.05). During dry season,* BOD_5 *ranged from 3.14 to 6.37 mg/L and COD ranged from 5.8–10.51 mg/L. In rainy season, the ranges were* BOD_5 *(2.88 – 6.10 mg/L) and COD (3.49–7.45 mg/L). Temperature ranged from 29.00 – 31.90* ^0C *in both seasons. Seasonal variations of the parameters were observed. BOD to COD ratio computed showed that some of the boreholes studied were highly polluted during dry season while all the boreholes studied were highly polluted during rainy season. The mean values of the parameters were compared with standard guideline values recommended by World Health Organisation (W.H.O.), Nigerian Standard for Drinking Water Quality (NSDWQ), National Agency for FOOD and Drug Administration and Control (NAFDAC). The mean values of* BOD_5 *as well as temperature in all the samples during both seasons were above the standard values, hence strongly indicative of negative bacteriological and thermal pollution indices.*

Keywords: *BOD, COD, groundwater pollution, Enugu north senatorial district.*

I. Introduction

Several millions of people have been reported dead globally due to drinking of polluted water caused by faecal pollution [1] which introduces harmful organic matter into the given body of water. Organic pollutants in groundwater also result from leachates or percolates from domestic sewage or industrial effluents. The organic matter content of water affects the level of its dissolved oxygen and can be determined by measurements of the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) of the water. BOD measures the amount of dissolved oxygen needed for the aerobic degradation (often by aerobic micro-organisms) of organic materials present in the water while COD measures the quantity of oxygen required for the chemical oxidation of pollutants in the water. Apart from the health implications of both water quality assessment parameters, BOD and COD constitute vital environmental significance in that they indicate the pollutant strength of polluted water. BOD measurement highlights the biodegradability and self-purification capacity of natural water such as groundwater. COD on the other hand highlights the strength of biologically resistant organic toxins in contaminated water. [2] BOD_5 describes a five-day test procedure in which the water sample is incubated throughout this period at controlled conditions. It is usually based upon comparison of the amount of initial dissolved oxygen (DO_1) and dissolved oxygen content in the sample at the end of the five-day period (DO_5). Apart from organic materials (such as the afore-mentioned faecal material), oxidizable nitrogen from its compounds also serve as food for aerobic bacteria and these as well as other chemically oxidizable materials such as iron (II) exert oxygen demand in the water in which they may be present. Apart from oxidizable materials, waste materials from domestic and industrial sources can also exert demand for oxygen. [3]

If the ratio of BOD: COD of wastewater or domestic water supply is found to be greater than or equal to a value of 0. 8, it is said to be highly polluted. [2] Therefore it is imperative that in the assessment of the quality of effluent water as well as domestic drinking water, BOD and COD determinations be conducted and their ratio computed on a routine basis.

Past studies on groundwater pollution as well as drinking water quality in South-east Nigeria have seldom emphasized the significance of BOD and COD measurements. Particularly in Enugu-north senatorial district, no single study have made BOD and COD seasonal routine determinations over a period of time a **central** focus. Hence there is a paucity of reliable baseline information on groundwater pollution due to biodegradable and biologically resistant oxidizable organic matter in the area.

II. Experimental

2.1 Study Area

The Study Area, Enugu North is one of the three senatorial districts in Enugu State, Nigeria. It comprises of seven Local Government Areas (LGAs) including Igbo Etiti, Igboeze North, Igboeze South, Isi-uzo, Nsukka, Udenu and Uzo-Uwani. As of 2007, Enugu North Zone had an estimated population of 1,377,001.[4]

Fig.1: Map of Enugu State, showing Study Area (Enugu North Senatorial District)

Table 1.1 Demographics of Enugu North Senatorial District

Uzo Uwani LGA	
•Headquarters:	Umulona.
•Coordinates:	6°45′N 7°12′E / 6.750°N 7.200°E
•Total Area	855 km^2 (330 sq mi)
•Total Population	124,480 [4]
Igbo Etiti LGA	
•Headquarters:	Ogbede.
•Coordinates:	6°40′N 7°22′E/6.667°N 7.367°E
• Total Area	325 km^2 (125 sq mi)
• Total Population	209,248 [4]
Udenu LGA	
•Headquarters:	Obollo-Afor.
•Coordinates:	6°55′N 7°31′E / 6.917°N 7.517°E
• Total Area:	248 km 2 (96 sq mi)
• Total Population:	178,466 [4]
Igbo Eze North LGA	
•Headquarters:	Enugu-Ezike.
•Coordinates:	6°59′N 7°27′E / 6.983°N 7.450°E
• Total Area:	293 km^2 (113 sq mi)
• Total Population:	259,431 [4]
Igbo Eze South LGA	
• Headquarters:	Ibagwa-Aka.
• Coordinates:	6°55′N 7°24′E / 6.917°N 7.400°E
• Total Area:	158 km 2 (61 sq mi)
• Total Population:	147,328 [4]
• Major economic activities:	Agriculture and trade.
•Climate:	

•Rainy season: March/April - October/November.
•Annual rainfall: varies from 1,400 mm to 2,000 mm
•Annual relative humidity during rainy season [at an average annual temperature above 20 °C (68.0 °F.)]: 75%
Humidity in the dry season: 90%

Nsukka LGA
Coordinates: 6°51′24″N 7°23′45″E / 6.85667°N 7.39583°E
• Total Area: 45.38 km^2 (17.52 sq mi)
Elevation: 1,810 ft (550 m)
• Total Population: 309,633 [4]
Isi Uzo LGA
Coordinates: 6°47′N 7°43′E / 6.783°N 7.717°E
• Total Area: 877 Km^2 (339 sq mi)
• Total Population 148,415 [4]
Headquarters: Ikem.

2.2 Sampling and Samples Determination

Borehole water was collected from twelve sample points covering the seven Local Government Areas in Enugu northern senatorial district and labelled for easy identification. The sampled boreholes were determined by spatial and depth distribution so as to allow reasonable distribution across and within the target area of study. Sampling operation was done so as to collect only representative samples for laboratory analyses. All sampling procedures as well as determinations of BOD, COD and temperature were performed using standard methods by the Association of Analytical Chemists (AOAC, 2005) and the American Physical and Health Association, American Water Works Association and Water Environment Federation (APHA-AWWA-WEF 2006). [2 and 3] Water used for blank determinations, dilution water (distilled water in an all-glass container), as well as all necessary Analar grade reagents were newly obtained from reputable standard laboratory supply companies. Instrumental calibrations were done following manufacturer's instructions. The samples were determined in triplicates on weekly bases for a period of six months covering two (dry and rainy) seasons. BOD and COD were tested by Winkler's incubation method and Titrimetric method (using a COD digester) respectively while temperature was measured using electrometric method (with a Hanna HI 9811-5 multi-meter).

III. Results and Discussion

Table 2.1 shows the summary of the results (mean ± SD values) as well as the ranges of BOD and COD in the 12 boreholes water samples during dry and rainy seasons.

Table 2.1: Mean ± SD and Range of the BOD_5 and COD values for rainy season and dry season.

Parameter	Season	Sample Designation									
		BH1		BH2		BH3		BH4		BH5	
		(ˣMean±SD)	ˣRange	(ˣMean±SD)	ˣRange	(ˣMean±SD)	ˣRange	(ˣMean±SD)	ˣRange	(ˣMean±SD)	ˣRange
BOD (mg/L)	Dry season	5.070±0.373	4.640-5.310	5.720±0.217	5.470-5.860	5.953±0.550	5.330-6.370	5.607±0.165	5.440-5.770	5.973±0.2122	5.800-6.210
	Rainy season	4.177±0.225	4.000-4.300	5.157±0.462	4.720-5.640	4.197±0.259	4.000-4.200	4.647±0.035	4.610-4.680	5.760±0.322	5.460-6.100
COD (mg/L)	Dry season	6.883±0.482	6.330-7.210	7.190±0.226	7.000-7.440	9.587±0.924	8.520-10.13	7.380±0.214	7.210-7.620	7.393±0.508	6.810-7.740
	Rainy season	5.007±0.140	4.870-5.150	6.550±0.235	6.320-6.790	4.937±0.280	4.760-5.260	5.447±0.404	5.100-5.890	7.047±0.542	6.430-7.450

Parameter	Season	Sample Designation									
		BH6		BH7		BH8		BH9		BH10	
		(ˣMean±SD)	ˣRange	(ˣMean±SD)	ˣRange	(ˣMean±SD)	ˣRange	(ˣMean±SD)	ˣRange	(ˣMean±SD)	ˣRange
BOD (mg/L)	Dry season	4.893±0.206	4.760-5.130	5.513±0.975	4.430-6.320	4.487±0.215	4.320-4.730	4.303±0.031	4.270-4.330	3.190±0.046	3.140-3.230
	Rainy season	4.037±0.210	3.800-4.200	2.950±0.062	2.880-3.000	4.023±0.078	3.960-4.110	3.970±0.177	3.780-4.130	4.400±0.174	4.200-4.520
COD (mg/L)	Dry season	8.670±1.339	7.710-10.20	9.230±2.140	6.760-10.51	6.180±0.308	5.840-6.440	6.430±0.118	6.330-6.560	6.617±0.342	6.230-6.880
	Rainy season	4.947±0.292	4.610-5.130	3.650±0.260	3.490-3.950	4.903±0.087	4.830-5.000	4.847±0.304	4.520-5.120	5.327±0.067	5.270-5.400

		BH11		BH12		(^{y}Mean±SD)	^{y}Range		Recommended Maximum Permissible Level
		(^{x}Mean±SD)	^{x}Range	(^{x}Mean±SD)	^{x}Range				
BOD (mg/L)	**Dry season**	5.593±0.038	5.550-5.620	5.560±0.157	5.450-5.730	5.155±0.822	3.140-6.370		*3.000
	Rainy season	4.413±0.042	4.380-4.460	3.730±0.057	3.680-3.790	4.288±0.703	2.880-6.100		
COD (mg/L)	**Dry season**	7.673±0.365	7.280-8.000	7.257±0.302	7.000-7.590	7.541±1.085	5.840-10.51		*294.0
	Rainy season	5.260±0.076	5.180-5.330	4.567±0.049	4.510-4.600	5.207±0.879	3.490-7.450		

Legend: BOD= Biochemical Oxygen Demand. COD= Chemical Oxygen Demand. BH= Borehole
^{x} is mean concentration and range of values for a given sample;
^{y} is mean concentration and range of values for all the 12 samples.
† Values are given by World Health Organisation (WHO).
***Values are given by National Agency for Food and drugs Administration and Control (NAFDAC).

3.1 BOD$_5$

During dry season, the lowest BOD$_5$ value of 3.140 mg/L was recorded in the water samples from BH10 and the highest value of 6.370 mg/L was recorded in BH3. The mean BOD$_5$ value for all the 12 boreholes water during dry season period was 5.155±0.822. During rainy season, BOD$_5$ ranged from 2.880 mg/L in BH7 to 6.100 mg/L in BH5. The mean BOD$_5$ value for all the 12 boreholes water during rainy season period was 4.288±0.703 as shown in Table 2.1. The higher BOD$_5$ mean value of 5.155±0.822 during dry season could be due to percolation of biodegradable organic matter and leaching of inorganic iron and/or manganese into groundwater aquifers. [5-7] Seasonal variations in BOD was observed with a general increase during dry season as shown in Fig.2. Recent findings from an assessment of selected groundwater samples from Amike-Aba, Abakaliki, south-east Nigeria also recorded a high BOD$_5$ range of 10.87 – 12.98 mg/L. [7] Also in 2012, findings on water supplies in Nsukka area, south-east Nigeria recorded a BOD range of 10.0 – 20.40 mg/L.[8] Several other studies within Nigeria and from around the world have reported high levels of BOD in ground water sources. [9–21] From the BOD$_5$ results in this study, it can be concluded that the ground water in the area studied is generally polluted due to high biochemical oxygen demand during dry season and rainy season periods and is unfit for drinking since the range of BOD$_5$ values is above the maximum permissible level of 3.00 mg/L recommended by National Agency for Food and drugs Administration and Control (NAFDAC) [22] and World Health Organisation (WHO) [23].

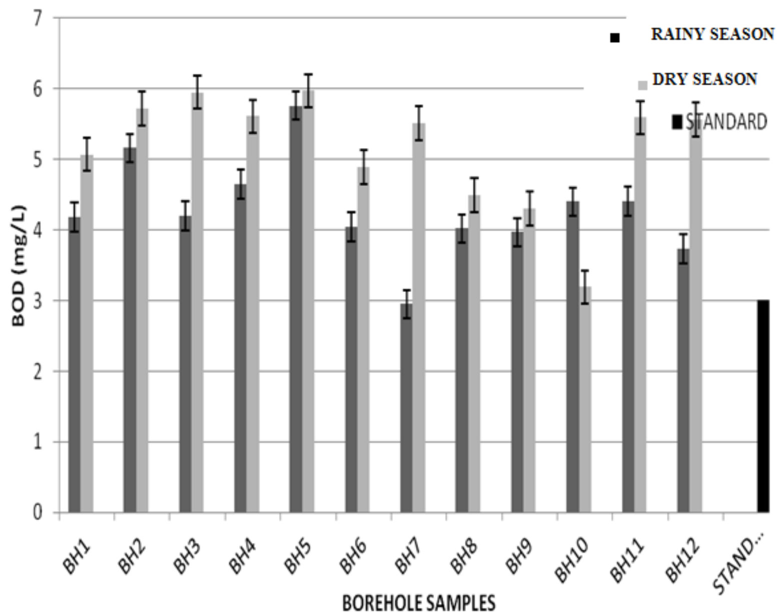

Fig. 2: Seasonal Variation in the BOD of the 12 boreholes.

3.2: COD

As shown in Table 2.1, the mean COD content was higher during dry season (7.541±1.085 mg/L) than at rainy season (5.207±0.879 mg/L) with values ranging from 5.840 mg/L (lowest in BH8) to 10.51 mg/L (highest in BH7) at dry season and 3.490 mg/L (lowest in BH7) to 7.450 mg/L (highest in BH5) at rainy season.

The higher mean COD content at dry season may be due to prolong accumulation of seeped organic leachates into the aquifers. A higher range of COD values than those in this study was obtained in a study that assessed the quality of boreholes located close to a dumpsite in Benin, south-south Nigeria. [20] The COD ranges in this study show similarity with COD range of 55.00 - 89.25 mg/L obtained in the assessment of water quality of boreholes around selected landfills in Kano Metropolis, northern Nigeria[24] as well as some selected boreholes in Umiahia in Abia state, south-east Nigeria [18] in that they are both below the recommended value set by the NAFDAC[22] and WHO[23]. Hence the observed pollution of the borehole water samples studied may not be due to chemical oxidation of pollutants present but due to aerobic degradation of organic matter present by micro-organisms in the water samples. Fig 3 shows the seasonal variation in COD in the 12 water samples studied.

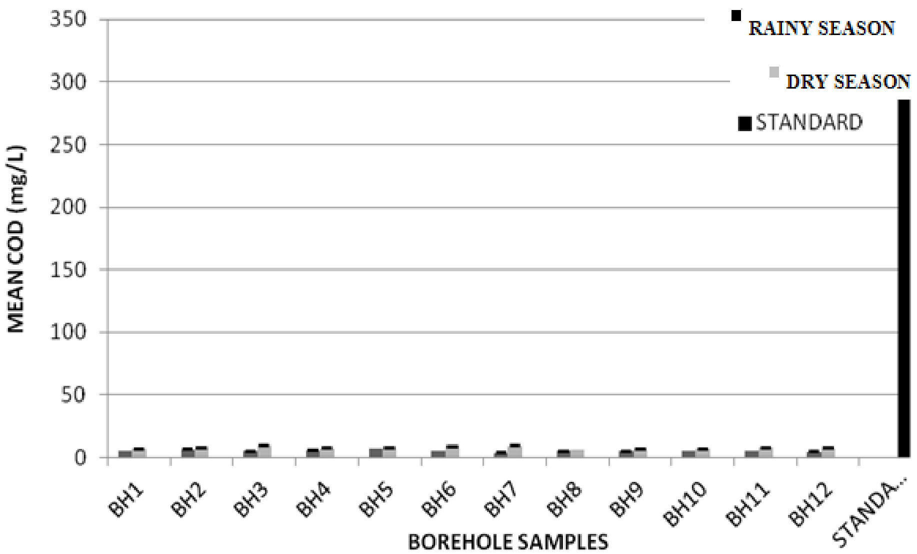

Fig. 3: Seasonal Variation in the COD of the 12 boreholes

3.3. BOD_5: COD Ratio

The ratios of BOD to COD values obtained during dry season and rainy season are presented in Table 2.2a and Table 2.2b respectively.

Table 2.2a: BOD_5: COD Ratio for the 12 boreholes during dry season.

Sample Designation	Dry season BOD (Mean±SD) (mg/L)	Dry season COD (Mean±SD) (mg/L)	Dry season BOD: COD Ratio	Pollution indication
BH1	5.070±0.373	6.883±0.482	0.74	Polluted
BH2	5.720±0.217	7.190±0.226	0. 80	Highly polluted
BH3	5.953±0.550	9.587±0.924	0.62	Polluted
BH4	5.607±0.165	7.380±0.214	0.76	Polluted
BH5	5.973±0.2122	7.393±0.508	0. 81	Highly polluted
BH6	4.893±0.206	8.670±1.339	0.56	Polluted
BH7	5.513±0.975	9.230±2.140	0.60	Polluted
BH8	4.487±0.215	6.180±0.308	0.73	Polluted
BH9	4.303±0.031	6.430±0.118	0.67	Polluted
BH10	3.190±0.046	6.617±0.342	0.48	Polluted
BH11	5.593±0.038	7.673±0.365	0.73	Polluted
BH12	5.560±0.157	7.257±0.302	0.77	Polluted

Table 2.2b: BOD: COD Ratio for the 12 boreholes during rainy season

Sample Designation	Rainy season BOD (Mean±SD) (mg/L)	Rainy season COD (Mean±SD) (mg/L)	Rainy season BOD: COD Ratio	Pollution indication
BH1	4.177±0.225	5.007±0.140	0.83	Highly polluted
BH2	5.157±0.462	6.550±0.235	0.79	Highly Polluted
BH3	4.197±0.259	4.937±0.280	0.85	Highly polluted
BH4	4.647±0.035	5.447±0.404	0.85	Highly polluted
BH5	5.760±0.322	7.047±0.542	0. 82	Highly polluted
BH6	4.037±0.210	4.947±0.292	0. 82	Highly polluted
BH7	2.950±0.062	3.650±0.260	0. 81	Highly polluted
BH8	4.023±0.078	4.903±0.087	0. 82	Highly polluted
BH9	3.970±0.177	4.847±0.304	0. 82	Highly polluted
BH10	4.400±0.174	5.327±0.067	0. 83	Highly polluted

BH11	4.413±0.042	5.260±0.076	0. 84	Highly polluted
BH12	3.730±0.057	4.567±0.049	0. 82	Highly polluted

As shown in the Table 2.2a above, BH2 and BH4 had BOD to COD ratio of 0.80 and 0.81 respectively during dry season. This indicates that the boreholes are highly polluted and are amenable to biological treatment since the values are equal to or greater than 0.80 [2; 25]. During rainy season, all the boreholes studied had BOD to COD ratio approximately 0.80 or greater than 0.80 (see Table 2.2b) indicating high pollution and amenability to biological treatment. [2; 25]

3.4 Temperature

The results of temperature analyses are summarized in Table 3. The highest temperature value of 31.90 ^{0}C observed, was the same for both dry season (in BH2) and rainy season (BH3) seasons. Lowest temperature recorded was 29.00 ^{0}C during dry season (BH9) and rainy season (BH1 and BH9). The mean temperatures were 30.44±0.746 and 30.32±0.848 during dry season and rainy season respectively indicating a slight decrease at rainy season. The slightly elevated values of temperature during dry season could be due to thermal storage of solar energy. A similar study reported a mean temperature of 25.4 ^{0}C in Ikare borehole in Kogi state, Nigeria lower than the mean temperature values observed in this study. [26] Temperature values obtained in this study were above ambient level (25^{0}C) recommended by the Nigerian Standard for Drinking Water Quality (NSDWQ), the Standard Organisation of Nigeria (SON) [27] thus indicates thermal pollution. The observed high level temperatures may be due to groundwater flow, heat transfer in porous groundwater media owing to geothermal gradient, thermal activity or geochemical sources such as acidic water in a highly alkaline soil causing exothermic reactions. The temperature variation in some of the boreholes could be as a result of differences in borehole depths, topography or nearness of boreholes to the thermal injection source such as power plants or due to the presence of micro- organisms in the water. Fig. 4 illustrates the seasonal variation in temperature values obtained across the 12 boreholes studied. Again as shown, the temperature values obtained during dry and rainy seasons were all above 25 ^{0}C. The elevated temperature values could also be due to microbial activity leading to high demand of dissolved oxygen. Water temperature has long been reported as being associated with dissolved oxygen [28] and largely determines the extent of microbial activity in the water. Birhanu (2007) illustrates the effect of coliforms on raw (untreated) drinking water temperature and showed that an increase in daily total coliforms (CFU/100 mL) causes a corresponding rise in monthly median temperature; hence temperature is critically a bacteriological related parameter [29] This study agree with the aforementioned finding since the high temperatures observed correspond with the generally high values of BOD obtained in the study.

Table 3: Mean ± SD and Range of the temperature values for rainy season and dry season.

Parameter	**Season**	**Sample Designation**									
		BH1		**BH2**		**BH3**		**BH4**		**BH5**	
Temp.(°C)	**Dry season**	**30.80±0.100**	**30.700-30.900**	**31.77±0.231**	**31.50-31.90**	**31.27±0.115**	**31.20-31.40**	**30.50±0.000**	**30.50-30.50**	**30.13±0.058**	**30.10-30.20**
	Rainy season	**29.07±0.058**	**29.00-29.10**	**30.13±0.058**	**30.10-30.20**	**31.77±0.115**	**31.70-31.90**	**30.13±0.058**	**30.10-30.20**	**29.90±0.346**	**30.80-31.00**

Parameter	**Season**	**Sample Designation**									
		BH6		**BH7**		**BH8**		**BH9**		**BH10**	
		(^{x}Mean±SD)	**^{x}Range**	**(^{x}Mean±SD)**	**^{x}Range**	**(^{x}Mean±SD)**	**^{x}Range**	**(^{x}Mean±SD)**	**^{x}Range**	**(^{x}Mean±SD)**	**^{x}Range**
Temp. (°C)	**Dry season**	30.73±0.058	30.70-30.80	29.90±0.173	29.80-30.10	29.87±0.289	29.70-30.20	29.03±0.058	29.00-29.10	30.10±0.000	30.10-30.10
	Rainy season	30.93±0.115	30.80-31.00	31.07±0.115	31.00-31.20	29.93±0.115	29.80-30.00	29.03±0.058	29.00-29.10	30.03±0.058	30.00-30.10

Parameter	**Season**								
		BH11		**BH12**		**(^{y}Mean±SD)**	**^{y}Range**		**Recommended Maximum Permissible Level**
		(^{x}Mean±SD)	**^{x}Range**	**(^{x}Mean±SD)**	**^{x}Range**				
Temp. (°C)	**Dry season**	**31.13±0.058**	**31.10- 31.20**	**30.03±0.058**	**30.00- 30.10**	**30.44±0.746**	**29.00-31.90**		**†*25.00(ambient)**
	Rainy season	**31.40±0.346**	**31.00-31.60**	**30.40±0.200**	**30.20- 30.60**	**30.32±0.848**	**29.00-31.90**		

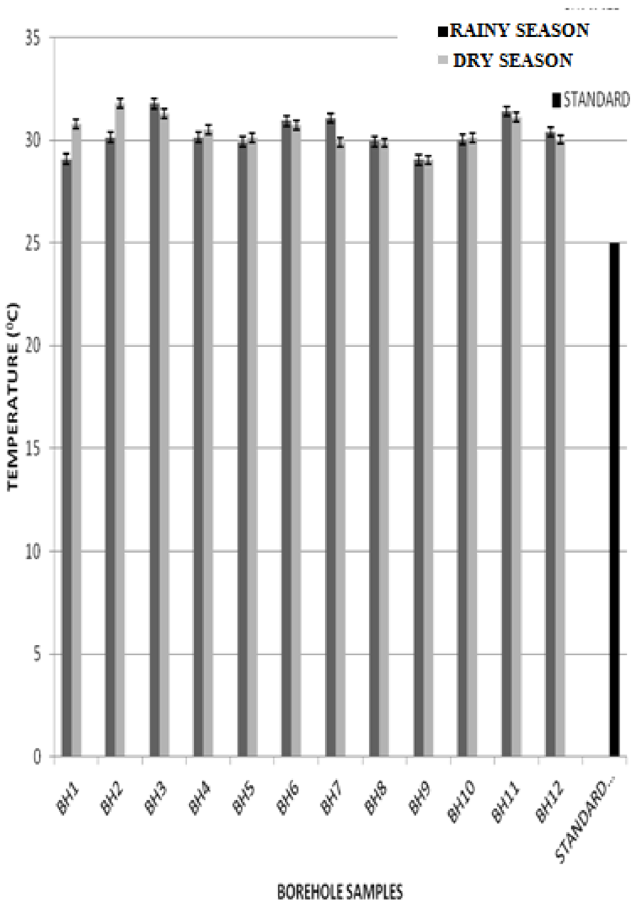

Fig. 4: Seasonal Variation in the temperature of the 12 boreholes

IV. Data Analysis

The data was summarised and presented in simple descriptive statistics (mean and standard deviations) as shown in Tables 2.1 and Table 3. A two-way ANOVA conducted revealed a statistically significant difference between the mean concentrations of parameters indicating general degree of pollution (BOD, COD and temperature) in the 12 boreholes water samples during dry season ($F(2, 33) = 2912.56$, $p < .05$). Post-hoc analyses of multiple comparisons using Dunett's T3 indicated a significant difference between the 12 water samples in terms of mean values of BOD ($p < .05$), COD ($p < .05$) and Temperature ($p < .05$) during dry season (See Appendix 1).

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APPENDIX 1: Descriptive Statistic (Anova) Comparing Dry Season Bod, Cod And Temperature In The 12 Water Samples.

Descriptive

PARAMETER SAMPLE

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
BOD (mg/L)	12	5.1553	.82151	.23715	4.6333	5.6772	3.19	5.97
COD (mg/L)	12	7.5408	1.08523	.31328	6.8513	8.2304	6.18	9.59
TEMPERATURE	12	30.4389	.74575	.21528	29.9651	30.9127	29.03	31.77
Total	36	14.3783	11.59259	1.93210	10.4560	18.3007	3.19	31.77

ANOVA

PARAMETER SAMPLE

PARAMETER VALUE	Equal variances assumed	36.413	.000	4.017	22	.001	4.43471
	Equal variances not assumed			4.017	11.068	.002	4.43471

Independent Samples Test

		t-test for Equality of Means		
		Std. Error Difference	95% Confidence Interval of the Difference	
			Lower	Upper
PARAMETER VALUE	Equal variances assumed	1.10389	2.14537	6.72404
	Equal variances not assumed	1.10389	2.00687	6.86255