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*Corresponding author

Abidemi O Omopariola, Institute of Ecology and Environmental Studies, Obafemi Awolowo University, Ile-Ife, Nigeria

email iD: abidemiomopariola@gmail.com

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Research Article

Evaluation of the Physico-Chemical Characteristics and Heavy Metal Contents of Shasha River, Southwestern Nigeria

Abidemi O Omopariola[1*], Funso I Adeniyi[2]

[1]*Institute of Ecology and Environmental Studies, Obafemi Awolowo University, Nigeria*

[2]*Department of Zoology, Faculty of Science, Obafemi Awolowo University, Nigeria*

Abstract

This study assessed the temporal and seasonal variations in the Physico-chemical and heavy metal concentrations of Shasha River. It also investigated the suitability of the water source for domestic uses and compared the water quality with the standard of drinking water provided by the World Health Organization and Nigeria Standard for Drinking Water Quality (WHO and NSDWQ). Three sampling stations A, B and C were selected along the channel of the river where it flowed across the zones in the study area. Water samples were collected from each of the station at every three months, giving a total of 12 samples over the two seasons of the annual cycle. The parameters investigated for include colour, turbidity, temperature, pH, electrical conductivity, alkalinity, acidity, ions, nutrient and oxygen compounds and trace metals. The results showed that approximately 60% of the water samples could be classified as soft fresh water type, which occurred within the range of Bromothymol blue (6.0 - 7.6) indicator. The water source was also characterized by high dissolved oxygen content (5.14 ± 2.64 mgL-1) and saturation (64.40 ± 32.87%), low nitrogen with moderate organic matter content. The result showed that the physico-chemical parameters were within the recommended limit except for colour turbidity and phosphate. All metals investigated for were present in the water samples, but none of the samples analysed had Zn concentration above the permissible limit, while Fe concentration was above the permissible limit for drinking water in 50% of the samples. Chromium, Ni, Cd, and Pb exceeded the limit for potable water in 100, 67.0, 92.0 and 17.0% respectively of the samples investigated. The study therefore concluded that considering the toxicity level of heavy metals, the water source is unreliable for drinking water supply purposes and would require some form of treatment.

Introduction

Water is an essential component for the survival of human life and the ecosystem in general [1, 2]. Therefore, we depend on a reliable and clean supply of drinking water to sustain our health. Water forms an important part of any nation's socio economic development, and therefore, cannot survive without it because of its vast use in other sectors of the economy [3-5]. It is a finite resource that is in high demand but has no substitute and too often, it carries pathogen-causing diseases and remains one of the most poorly managed resources on earth. Water development, use and management have been one of the world's challenge and made it to the list of priorities for 2030 Agenda for sustainable development, and has brought water quality issues to the attention of international community thereby setting a specific goal in (SDG 6: ensure availability and sustainable management of water and sanitation for all [6]. In many countries, the quantity and quality of surface resources are declining faster than attention is been given to mitigating and conserving the resource hence posing a threat to water availability and use for the future generation. Many of these uses put pressure on our water environment due to increased industrialization, which in turn has enhanced urbanization and thus on the high rise and ultimately changed natural ecosystems and water quality, thereby reducing the availability of clean water to end users; challenges which might be exacerbated by climate change [3, 7]. Human beings, animals, organisms, and the ecosystems are all affected by contaminated water [8]. Among the different pollution types, water pollution, has a major threat to human health [9, 4] and is one of the most remarkable concern for sustainable development. Moreover, the microbiological contamination of water does not only cause child mortality, but also repeated attack of diarrhea among children aged less than two years, impair cognitive development and school performance among survivors [10]. Thus, inadequate or lack of provision of clean and safe water to the ever increasing population implies increase in childhood deaths, less cognitive development, less educational achievement, and less economic growth. Several studies have reported the impact of drought on water quality, [11] that mainly include increased pollutant concentration, enhanced nitrogen mineralization, and delayed recovery from acidification. According to the studies [12, 7], human activities mainly affect surface water quality through effluent discharges, use of agricultural chemicals and in addition increased exploitation of water resources. These activities have been reported of contributing to the poor quality of some rivers in Nigeria, especially in the Niger delta area [13]. Rivers in developing countries may be heavily polluted due to anthropogenic activities [14]. In this part of the world, rivers are seen and used as channels for disposing off solid and liquid waste because of poor or lack of adequate waste management systems. In recent times, the world has realized the relationship between water and water borne diseases as a crucial public health issue [4]. Therefore, assessing river quality is essential to the sustenance of aquatic biodiversity, the environment and public health [15]. Heavy metals are also of great consideration in terms of water quality because industrialization has increased the spread of environmental contamination by heavy metals. Although, trace metals such as lead, cadmium, chromium, zinc, iron, nickel, and copper, are present in the environment, excess concentration can be potentially toxic to the biota and affect humans greatly. Several studies on Nigerian surface water have been investigated [4, 16-20]. The works of the study [21] also reported that industrial activity and its effluent have contaminated Njaba River with large amount of heavy metals. Continuous discharge of domestic sewage and solid waste dump and industrial effluents, over time into surface water can cause the groundwater to become polluted through stream flow and create health problems [9, 22]. It is therefore crucial that the surface waters that abound in Nigeria are investigated with continuous surveillance and monitoring of their quality. This study was carried out to access the heavy metal content and the physicochemical water quality of Shasha River.

Study Area

The river Shasha has its source from Ogun-Osun river basin, in the rain forest zone of Nigeria [23]. The drainage system of river Osun rises from Oke Mesi ridge, approximately 5km North of Effon Alaiye those boarders between Osun and Ekiti States

Table 1: Descriptive statistics of the physico-chemical parameters of surface water quality.

Parameters (unit)	N	Minimum	Maximum	Mean	Median	Standard Error of Mean	Standard Deviation	Skewness	Kurtosis	%Coefficient of Variance
Physical Parameter										
Air Temperature (oC)	12	24	33	28.79	28.25	0.81	2.81	0.01	-1.01	9.75
Water Temperature (oC)	12	22.5	30.5	26.92	26.5	0.67	2.3	-0.21	-0.3	8.56
Apparent Color (Pt-Co)	12	46.08	1222.44	304.49	111.04	121.2	419.85	1.94	2.35	137.89
True Color (Pt-Co)	12	42.1	742.28	198.96	90.25	69.87	242.03	1.94	2.47	121.65
Turbidity (NTU)	12	57.39	67.17	61.89	60.87	0.88	3.05	1.97	-0.74	4.92
Static Water Depth (m)	12	0.04	1.49	0.57	0.56	0.13	0.43	0.58	0.22	75.83
Total Water Depth (m)	12	0.92	2.1	1.42	1.39	0.1	0.35	0.58	0.27	24.78
Water Column Depth (m)	12	0.36	1.53	0.85	0.83	0.11	0.38	0.58	-0.4	44.76
General Chemical Parameters										
pH (pH Unit)	12	6.97	7.97	7.52	7.6	0.09	0.34	-0.23	-1.38	4.53
Conductivity (μScm^{-1})	12	87.4	221	153.22	161.5	10.56	36.56	-0.02	0.11	23.86
TDS (mgL^{-1})	12	58.1	152	106.53	110.8	7.17	24.85	-0.3	0.59	23.33
Alkalinity (mgCaCO3 L^{-1})	12	40	100	72.5	75	6.03	20.89	-0.21	-1.19	28.82
Acidity (mgCaCO3 L^{-1})	12	4	28	13	13	1.96	6.8	0.72	0.96	52.27
Major Ions										
Calcium (Ca2^{+}) (mgL^{-1})	12	9.04	25.28	17.62	18.64	1.23	4.27	-0.28	0.61	24.23
Magnesium (Mg^{2+})(mgL^{-1})	12	0.2	5.95	3.26	4.21	0.6	2.09	-0.33	-1.57	64.22
Potassium (K^{+}) (mgL^{-1})	12	1.59	3.3	2.37	2.24	0.14	0.5	0.37	-0.33	21.07
Sodium (Na^{+}) (mgL^{-1})	12	0.1	3.45	1.98	2.28	0.35	1.23	-0.68	-0.99	62.12
Sulphate (SO4$^{2-)}$ (mgL^{-}1)	12	0.47	54.54	17.06	13.5	4.98	17.25	1.2	0.76	101.13
Chloride (Cl^{-}) (mgL^{-1})	12	1.44	16.28	9.71	9.64	1.18	4.1	-0.34	0.12	42.22
HCO3- (mgL^{-1})	12	48	120	87	90	7.24	25.07	-0.21	-1.19	28.82
Hardness (mgCaCO3 L^{-1})	12	46.05	68.03	58.03	60	2.06	7.15	-0.4	-0.85	12.32
Heavy Metal parameters										
Iron (mgL^{-1})	12	0.34	1.66	0.81	0.67	0.13	0.46	1	-0.17	56.69
Zinc (mgL^{-1})	12	0.08	0.43	0.26	0.25	0.04	0.13	0.05	-1.88	53.33
Cadmium (mgL^{-1})	12	0	0.03	0.02	0.02	0	0	-0.14	-0.77	55.16
Chromium (mgL^{-1})	12	0.06	0.26	0.14	0.11	0.02	0.07	0.69	-1.1	52.85
Lead (mgL^{-1})	12	0	0.02	0.01	0.01	0	0.01	0.26	-0.69	86.13
Nickel (mgL^{-}1)	12	0.02	0.41	0.18	0.13	0.04	0.14	0.55	-1.26	80.65
Nutrient Compounds										
Nitrate (NO_3) (mgL^{-1})	12	0.02	1.6	0.41	0.12	0.14	0.5	1.45	1.63	121.79
Phosphate (PO4^{3}-) (mgL^{-1})	12	0.23	17.8	6.13	2.25	1.87	6.48	0.58	-1.44	105.69
Silica (SiO2) (mgL-1)	12	0.08	1.6	0.54	0.41	0.12	0.42	1.6	3.01	77.43
Organic Matter (mgL-1)	12	0.45	14.72	6.01	3.42	1.55	5.37	0.56	-1.51	89.37
Oxygen Parameters										
Dissolved Oxygen (mgL-1)	12	0.95	8.8	5.14	5.5	0.76	2.64	-0.49	-1	51.29
COD (mgL-1)	12	0	50.29	17.17	17.85	3.88	13.44	1.3	2.55	78.28
BOD (mgL-1)	12	1.2	6.4	3.35	3.3	0.41	1.42	0.4	0.99	42.43
DOS (%)	12	11.38	113.99	64.4	70.65	9.49	32.87	-0.5	-0.73	51.04

N= No of Samples COD= Chemical Oxygen Demand, BOD= Biologic Oxygen Demand, DOS = Dissolved Oxygen Saturation of Nigeria. It drains westward through Osogbo, the Osun state capital and flows through Ede into Odeomu, Gbongan and Orile-owu towns in Ayedaade Local Government Area (Figure 1). The stretch of the river lies within Latitudes 07°12' 20" - 07 °36' 13" N and Longitudes 004 °16' 57" - 004 ° 24' 36" E. The area is underlain by the metamorphic Basement Complex rocks and are mainly undifferentiated consisting of two major rock types these are; the migmatite complex (including banded magmatic and auguen gneisses and pegmatites); and meta-sediments (schist and quartzite, quartzofelspartic rock, calsilicate, meta-conglomerates, amphibolites and metamorphic iron beds [24, 9]. The climate type is tropical wet and dry, according to Koppen classification [25] and experiences two types of seasons; dry and rainy seasons. Rainfall occurs between the months of April to October, and peaks in July while the dry season occurs from November to March.

Sample collection and sample procedure

Water samples were collected from three selected sampling stations A, B and C at every three months, covering the dry and rainy seasons of the annual cycle (March - December 2017) along the river channel. Twelve (12) water samples were collected from the study area in well-labelled 2 liters sample bottles. During sampling, the bottles were washed with soap, rinsed in clean water, thereafter rinsed with the sample water before filling, and tightly closed immediately. Samples were also collected for oxygen parameters in DO and BO5 bottles and fixed in the field with potassium iodide (KI) and Manganese Sulphate ($MnSO_4$). The samples were transported in a box with ice packs to the laboratory and stored at low temperature (4°C) for the Physico-chemical analysis and metal ion concentrations with samples preserved using nitric acid. Standard methods were used with adequate quality assurance and quality control measures.

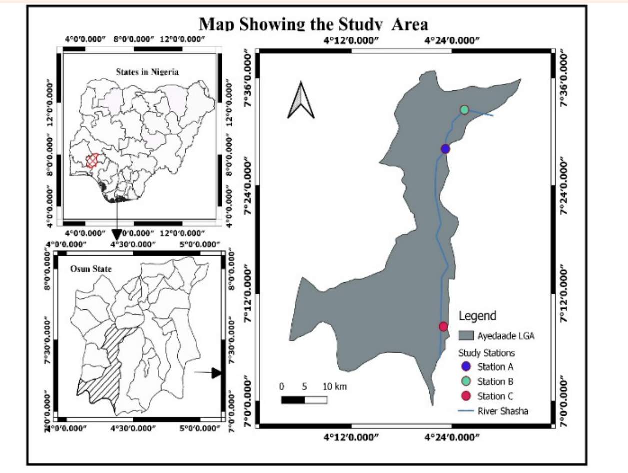

Figure 1: Map of the Study area.

Methodology

The water and air temperatures were determined in-situ in the field using mercury in glass bulb thermometer. A multi-parameter device (PCE-PHD1) was used to determine the pH, conductivity and TDS. Winkler titration was used for DO and BOD5 while alkalinity, acidity, calcium, magnesium, and total hardness were determined titrimetrically, using standard methods by Golterman, Ademoroti and APHA [26-28]. Colour, turbidity, phosphate and nitrate were determined colorimetrically using Jenway colorimeter, model 6051. Organic matter was by wet digestion method and trace metals were analyzed using Atomic Absorption Spectrophotometry (AAS) using model PG990. For each heavy metal, specific concentration standard was run to prepare a calibration curve from which the concentration of the heavy metal was read directly from the AAS. The data obtained were subjected to appropriate descriptive, inferential statistics (ANOVA) as applicable. The statistical software used was PAST version 2.17, and Excel, 2016.

Results and Discussion

Physical and meteorological parameters

The total ambient air temperature from river Shasha varied from 24oC to 33oC with an overall mean value of 28.79 ± 0.81oC while water temperature varied from 22.5 to 30.5oC and falls within the optimum thermal values for tropical freshwater with an overall mean value of 26.92 ± 0.67oC (Table 1). The air and water temperatures across the stations recorded the lowest mean value at station B and the highest mean value at station C. The air temperature was higher than the water temperature, which may be because of the tree canopy across the river channel that provided shade, reduced the sunlight intensity from directly reaching the water surface, and kept the temperature low. Air temperature range and mean value during the dry season was 26 oC to 33 oC and 29.50 ± 1.28 oC while the rainy season values were 24 oC to 31 oC and 28.08 ± 1.02 oC. The dry season temperature was higher than the rainy season because of the rise in sunlight intensity and heat absorption (Table 2). Water temperature range for dry and rainy seasons respectively were 22.5 oC to 30.5 oC and 24.50 oC to 29.00 oC while the respective mean values were 27.42 ± 2.97oC; 26.42 ± 1.50oC (Table 2). The mean water temperature was lower in the rainy season and this was attributed to cloud cover, precipitation and prevailing air masses bringing in moist air over the area. On the other hand, higher temperature experienced in the dry season was due to an increase in sunlight intensity with reduced humidity, and ultimately leading to increased metabolic activities in the water. This observation was similar with the works of the researcher [16] who studied the seasonal variation of water quality in kwanda LGA of Benue State. The air and water temperatures showed a significant difference ($p \leq 0.05$) in mean values between the two seasons (Table 2). The overall apparent colour ranged from 46.08 to 1222.44 Pt-Co with a mean value of 304.49 ± 419.85 Pt-Co, while the true color ranged from 42.10 to 742.28 Pt-Co with a mean value of 198.96 ± 242.03 Pt-Co (Table 1). The highest value (1222.44 Pt-Co) was recorded at station A, while the lowest value was recorded at station C. The presence of colour was due to dissolved minerals and organic matter in the water. During the dry season, the apparent colour ranged from 46.08 Pt-Co to 1222.44 Pt-Co with a mean value of 509.87 ± 218.50 Pt-Co and the rainy season range and mean values were 82.55 Pt-Co to 114.17 Pt-Co and 99.12 ± 4.82 Pt-Co (Table 2). The mean apparent value was higher in the dry season relative to the rainy season which might have been caused by increased municipal waste dumps, and washing activities in the river. Although the rainy season value too was high, dilution effect from rainfall and rate of flow could have contributed in reducing the colour concentration. Apparent colour showed a significant difference ($p \leq 0.05$) in mean values between the two seasons (Table 2). The overall range value of turbidity was 57.39 to 67.17 NTU with a mean value of 61.89 ± 0.88 NTU (Table 1). This range was recorded during the dry season. The lowest mean turbidity value of (59.14 ± 0.61 NTU) was recorded from station C, while the highest mean value (63.32 ± 1.40 NTU) was recorded from station A. During the rainy season, values ranged from 59.12 to 61.64 NTU while the mean values for rainy and dry seasons were 60.44 ± 0.91 and 63.34 ± 3.82 NTU respectively (Table 2).

Table 2: ANOVA Statistics of the Seasonal variation in physical parameters of surface water quality

Parameters (unit)	N	Dry Season	Rainy Season	ANOVA	
		Mean ± S.E	Mean ± S.E	F	P
Physical Parameter					
Air Temperature (°C)	6	29.5±1.28	28.08±1.02	14.45	0.019*
Water Temperature (°C)	6	27.42±1.21	26.42±0.61	36.06	0.003**
Apparent Colour (Pt-Co)	6	509.86±218.49	156.99±26.81	7.744	0.050*
True Colour (Pt-Co)	6	313.56±127.34	84.35±2.90	6.941	0.058
Turbidity (NTU)	6	63.34±1.56	60.44±0.37	2.725	0.174
Static Water Depth (m)	6	0.86±0.15	0.28±0.12	0.417	0.553
Total Water Depth (m)	6	1.55±0.16	1.29±0.11	0.11	0.758
Water Column Depth (m)	6	0.69±0.18	1.01±0.10	0.015	0.908

*= Significant difference ($p \leq 0.05$) ** = highly significant difference ($p \leq 0.01$) *** = Very highly significant difference ($p \leq 0.001$)

The dry season mean value was higher than the rainy season; this observation was a deviation from the norm. A possible reason for this could be the daily stir of the shallow river bottom from the different human activities, herders and possible runoffs from the catchment that washed off soil particles, silts and clay minerals back into the river. The mean values were not significantly different ($p \geq 0.05$) between the two seasons of the annual cycle. The values obtained were above the acceptable limit of 5 NTU by WHO and NSDWQ [29, 30]. The water table depth ranged from 0.04 to 1.49 m with a mean value of 0.57 ± 0.13 m while the total depth ranged from 0.92 to 2.10 m with a mean value of 1.42 ± 0.10 m (Table 1). The shallowest was station A, with a mean value of 1.21 ± 0.12 m and the deepest was station C with a mean of 1.63 ± 0.27 m. The water column depth range and mean values were 0.36 to 1.53 m and 0.85 ± 0.11 m (Table1). The water table depth ranged from 0.04 to 1.49 m during the dry season and 0.04 to 0.77 m in the rainy season with mean values of 0.86 ± 0.15 m and 0.28 ± 0.12 m respectively (Table 2). The Total depth of the river ranged from 1.2 to 2.10 m with a mean value of 1.55 ± 0.16 m in the dry season and ranged from 0.92 to 1.59 m with a mean value of 1.29 ± 0.29 m during the rainy season. The water column depth ranged from 0.36 to 1.53 m with a mean value of 0.69 ± 0.44 m in the dry season while values ranged from 0.76 to 1.47 m with a mean value of 1.01 ± 0.26 m in the rainy season (Table 2). There was no significant difference ($p \geq 0.05$) between the seasons.

Table 3: ANOVA Statistics of the Seasonal variation in chemical parameters of surface water quality.

Parameters (unit)	N	Dry Season	Rainy Season	ANOVA	
		Mean ± S.E	Mean ± S.E	F	P
General Chemical					
pH (pH Unit)	6	7.73 ± 0.09	7.30 ± 0.12	7.37	0.022*
Conductivity (µScm^{-1})	6	180.42 ± 9.37	126.02 ± 10.32	15.23	0.003**
TDS (mgL^{-1})	6	122.72 ± 6.44	90.35 ± 8,96	8.604	0.015*
Alkalinity (mgCaCO$_3$ L^{-1})	6	90.00 ± 3.65	55.00 ± 4.92	32.64	0.0001948***
Acidity (mgCaCO$_3$ L^{-1})	6	12.67 ± 1.84	13.33 ± 3.68	0.02632	0.874

*= Significant difference ($p \leq 0.05$) ** = Highly significant difference ($p \leq 0.01$) *** = Very highly significant difference ($p \leq 0.001$)

Table 4: ANOVA Statistics of the Seasonal variation in ionic parameters of Shasha River.

Parameters (unit)	N	Dry Season	Rainy Season	ANOVA	
		Mean ± S.E	Mean ± S.E	F	P
Major Ions					
Calcium (Ca^{2+}) (mgL^{-1})	6	17.10 ± 1.90	18.15 ± 1.72	0.1665	0.692
Magnesium ($Mg2^{+}$)(mgL^{-1})	6	4.32 ± 0.72	2.20 ± 0.80	3.888	0.077
Potassium (K^{+}) (mgL^{-1})	6	2.47 ± 0.28	2.27 ± 0.10	0.4735	0.507
Sodium (Na^{+}) (mgL^{-1})	6	2.54 ± 0.31	1.41 ± 0.57	2.963	0.116
Sulphate (SO_4^{2}-) (mgL^{-1})	6	21.33 ± 9.68	12.79 ± 2.85	0.7169	0.417
Chloride (Cl^{-}) (mgL^{-1})	6	11.33 ± 1.42	8.08 ± 1.76	2.074	0.18
HCO3- (mgL^{-1})	6	108.00 ± 4.38	66.00 ± 5.90	32.64	0.0001948***
Hardness (mgC$_a$CO$_3$ L^{-1})	6	60.46 ± 3.17	55.59 ± 2.52	1.448	0.2566

* = Significant difference ($p \leq 0.05$) ** = highly significant difference ($p \leq 0.01$) *** = Very highly significant difference ($p \leq 0.001$)

Table 5: ANOVA Statistics of the Seasonal variation in heavy metal parameters of shasha River.

Parameters (unit)	N	Dry Season	Rainy Season	ANOVA	
		Mean ± S.E	Mean ± S.E	F	P
Heavy Metal parameters					
Iron (mgL^{-1})	6	0.94 ± 0.25	0.68 ± 0.08	0.985	0.3444
Zinc (mgL^{-1})	6	0.23 ± 0.05	0.29 ± 0.06	0.4575	0.5141
Cadmium (mgL^{-1})	6	0.02 ± 0.00	0.02 ± 0.00	0.7895	0.3951
Chromium (mgL^{-1})	6	0.12 ± 0.02	0.15 ± 0.04	0.6932	0.4245
Lead (mgL^{-1})	6	0.01 ± 0.00	0.01 ± 0.00	3.077	0.1099
Nickel (mgL^{-1})	6	0.23 ± 0.07	0.13 ± 0.04	1.477	0.2522

*= Significant difference ($p \leq 0.05$) = highly significant difference ($p \leq 0.01$) **= Very highly significant difference ($p \leq 0.001$)

Table 6: ANOVA Statistics of the Seasonal variation in nutrient and oxygen parameters of surface water.

Parameters (unit)	N	Dry Season	Rainy Season	ANOVA	
		Mean ± S.E	Mean ± S.E	F	P
Nutrient Compounds					
Nitrate (NO3) (mgL^{-1})	6	0.75 ±0.21	0.07 ±0.02	10.85	0.0081**
Phosphate (PO_4^{3-}) (mgL^{-1})	6	5.28 ±3.03	6.99 ±2.44	0.192	0.6705
Silica (SiO_2) (mgL^{-1})	6	0.71 ±0.21	0.37 ±0.10	2.095	0.1784
Organic Matter (mgL^{-1})	6	4.51 ±2.30	7.51 ±2.09	0.9274	0.3582
Oxygen Parameters					
Dissolved Oxygen (mgL^{-1})	6	5.77 ±0.57	4.52 ±1.44	0.6526	0.438
COD (mgL^{-1})	6	21.10 ±7.30	13.24 ±2.60	1.028	0.335
BOD (mgL^{-1})	6	3.27±0.28	3.44±0.81	0.01414	0.843
DOS (%)	6	72.08 ±5.79	56.72 ±18.41	0.6334	0.445

COD= Chemical Oxygen Demand BOD= Biologic Oxygen Demand DOS = Dissolved Oxygen Saturation, *= Significant difference ($p \leq 0.05$) ** = highly significant difference ($p \leq 0.01$) *** = Very highly significant difference ($p \leq 0.001$)

General chemical parameters

The pH value ranged from 6.97 to 7.97 pH unit but on the average, showed a slightly alkaline condition with an overall mean value of 7.52 ± 0.34 pH unit (Table 1). The lowest pH value of 6.97 was recorded in station B and the highest value of 7.97 in station A. The dry season pH value ranged from 7.35 to 7.97 with a mean value of 7.73 ± 0.23 pH unit and ranged from 6.97 to 7.77 with a mean value of 7.30 ± 0.30 in the rainy season (Table 3, Figure 2). The higher pH mean value (7.73) in the dry season indicated more waste from different sources into the river. On the other hand, the lower mean value of (7.30) in the rainy season suggested reduced anthropogenic activities and dilution effect from rainfall. The average mean value of 7.52 ± 0.34 pH unit made the water conducive for fish production [31], and suitable for other domestic uses. Hence, the values obtained were within the permissible limits of 6.5 - 8.5 for natural water by WHO and NSDWQ. There was a significant difference ($p \leq 0.05$) between the two mean seasonal values (Table 3 and Figure 2). The electrolytic conductivity ranged from 87.40 µScm^{-1} in station B to 221 µScm-1 in Station C. The magnitude of conductance in the samples was in the order; station B < station A < station C, with an overall mean value of 53.22 ± 36.56 µScm^{-1} (Table 1). The range value of electrolytic conductivity during the dry season was 163.00 to 221.00 µScm^{-1} with a mean value of 180.42 ± 9.37 µScm^{-1} while 87.40 to 160.00 µScm^{-1} with a mean value of 126.02 ± 10.32 µScm^{-1} was recorded in the rainy season. It was observed that the seasonal mean value of electrolytic conductivity was higher in the dry season than

Table 7: Comparison of the surface water with the standards for drinking water and general uses.

Parameter (Unit)		*WHO 2011	**NSDWQ 2007	Range values of samples	% of samples within permissible level
General physical parameter	Air Temp (oC)	NG	NG	24.00-33.00	NG
	Water Temp (oC)	NG	NG	22.5-30.50	NG
	Apparent Colour (Pt - Co)	50	20	46.08-1222.44	8**
	True Colour (Pt - Co)	15	15	42.10-742.28	8*
	Turbidity (NTU)	5	5	57.39-67.17	0
General chemical parameters	PH (pH unit)	6.5 – 9.2	6.5-8.5	6.97-7.97	100*
	Conductivity (μScm^{-1})	NG	1000	87.40-221.00	100**
	TDS (mgL^{-1})	NG	500	58.10-152.00	100**
	Alkalinity (mgCaCO3 L^{-1})	500	NG	40.00-100.00	100*
	Acidity (mgCaCO3 L^{-1})	NG	NG	4.00-28.00	NG
Major ions	Ca^{2+} (mgL^{-1})	200	NG	9.04-25.28	100*
	Mg^{2+} (mgL^{-1})	150	NG	0.20-5.95	100*
	K^{+} (mgL^{-1})	NG	NG	1.59-3.30	NG
	Na^{+} (mgL^{-1})	200	200	0.10-3.45	NG
	SO_4^{2-} (mgL^{-1})	250	100	0.47-54.54	100*
	Cl- (mgL^{-1})	200	250	1.44-16.28	100*
	HCO^{3-} (mgL^{-1})	NG	NG	48.00-120.00	NG
	Hardness ($mgCaCO_3$ L^{-1})	NG	150	46.05-68.03	100*
Trace/Heavy metals	Iron Fe^{2+} (mgL^{-1})	0.3	0.3	0.34-1.66	100*
	Zinc (mgL-1)	NG	3	0.08-0.43	50**
	Cadmium (mgL^{-1})	0.003	0.003	0.01-0.03	8*
	Cr (mgL^{-1})	0.05	0.05	0.06-0.26	0**
	Lead (mgL^{-1})	0.01	0.01	0.00-0.02	83*
	Nickel (mgL^{-1})	0.07	0.02	0.02-0.41	33*
Nutrient compounds	Nitrate (NO^{3-}) (mgL^{-1})	50	50	0.02-1.60	100*
	Phosphate (PO43-) (mgL^{-1})	NG	NG	0.23-17.80	NG
	Silica (mgL^{-1})	NG	NG	0.26-1.60	NG
	Organic Matter (mgL^{-1})	NG	NG	0.45-14.72	NG
Oxygen parameters	Dissolved Oxygen (mgL^{-1})	NG	5	0.95-8.80	42
	COD (mgL^{-1})	NG	NG	0.00-50.29	NG
	BOD (mgL^{-1})	NG	≤ 6	1.20-19.60	92
	DOS (%)	NG	NG	11.38-113.99	NG

Source: *WHO guideline for drinking water (2011) **NSDWQ guideline for drinking water (2007) NG = No guideline

in the rainy season and this indicated high dissolved solid in the water due to evaporation effect [18]. There was a significant difference ($p \leq 0.05$) over the two seasons of the annual cycle (Table 3). The range and mean values of the total dissolved solid were 58.10 to 152.00 mgL^{-1} and 106.53 ± 7.17 mgL^{-1} respectively. A plot of the concentration of TDS and conductivity shows that conductivity was directly proportional to the concentration of the TDS. Both concentrations were within the recommended drinking water standards. The range and mean values of TDS during the dry season were 109.60 to 152.00 mgL^{-1} and 122.72 ± 6.44 mgL^{-1} while the range and mean TDS values in the rainy season were 58.10 to 120.00 mgL^{-1} and 90.35 ± 8.96 mgL^{-1} respectively. The TDS concentration was higher in the dry season than in the rainy season. This probably was because of increased sunlight intensity that resulted in the river drying up by evaporation, which caused an accumulation of organic and inorganic substance during the dry season [18]. The seasonal mean values were significantly different ($p \leq 0.05$) in the rainy season than in the dry season. The total acidity range and mean values ranged from 4.00 to 28.00 $mgCaCO_3L^{-1}$ and 13.00 ± 1.96 $mgCaCO_3L^{-1}$ respectively. The lowest value was recorded from station C, and highest value at station B. In the dry season, the range and mean values for acidity was 8.00 to 20.00 $mgCaCO_3L^{-1}$ and 12.67 ± 1.83 $mgCaCO_3L^{-1}$ respectively, while the acidity range and mean values in the rainy season was 4.00 to 28.00 $mgCaCO_3L^{-1}$ and 13.33 ± 3.68 $mgCaCO_3L^{-1}$ respectively. Although acidity value was higher in the rainy season than in the dry season, there was no significant seasonal mean difference ($p \geq 0.05$) over the annual cycle. Alkalinity concentration value ranged from 40 to 100 $mgCaCO_3L^{-1}$ with a mean value of 72.5 ± 6.03 $mgCaCO_3L^{-1}$. The mean alkalinity value was higher in the dry season (90.00 ± 3.65 $mgCaCO_3L^{-1}$) than in the rainy season (55.00 ± 4.92 $mgCaCO_3L^{-1}$). Alkalinity shows the ability of water to increase the pH of the soil and the buffering power of water itself. In addition, it is an indicator to the nature of the rocks within an aquifer and the extent to which they have been weathered to release metals [32]. There was a significant difference ($p \leq 0.05$) between the two seasons. However, the coefficient of variation was higher in the rainy season than in the dry season.

Major ion parameters of water quality

The overall calcium range and mean values were 9.04 to 25.28 mgL^{-1} and 17.62 ± 1.23 mgL^{-1} respectively (Table 1). Calcium ion was highest at station An in June and lowest at Station B in December. Calcium concentration during the rainy season ranged from 13.47 to 25.28 mgL^{-1} with a mean value of 18.15 ± 1.72 mgL^{-1} whilst the dry season range and mean values were 9.04 to 22.07 mgL^{-1} and 17.10 ± 1.90 mgL^{-1} (Table 4 and Figure 3). The rainy season value was higher but the seasonal mean values were not statistically different ($p \geq 0.05$) (Table 2). Calcium is a soft metal; the surrounding rocks in the area are rich in biotite and Meta sediments, which are abundant in calcium silicate minerals. Precipitation effect on rock weathering therefore enhanced the dissolution of calcium ions, hence the observed increase in concentration. Magnesium ion overall concentration ranged from 0.2 to 5.95 mgL^{-1} with a mean value of 3.26 ± 0.60 mgL^{-1} (Table 1). Magnesium concentration during the rainy season ranged from 0.20 to 4.79 mgL^{-1} with a mean value of 2.20 ± 0.80 mgL^{-1} while the dry season range and mean values were 1.06 to 5.95 mgL^{-1} and 4.32 ± 0.72 mgL^{-1} (Table 4 and Figure3). High concentration of calcium and magnesium in water is known to be responsible for water hardness. However, in the present study, magnesium concentration was generally low across the seasons and this probably explains why the water was classified as soft fresh water type. There was no significant difference ($p \geq 0.05$) observed between the two mean values Overall potassium concentration ranged from 1.59 to 3.30 mgL^{-1} with a mean value of 2.37 ± 0.50 mgL^{-1}. The lowest value was recorded at station C while station A recorded the highest value. During the rainy season, its concentration ranged from 2.07 to 2.75 mgL^{-1} with a mean value of 2.27 ± 0.10 mgL^{-1} while the dry season concentration range and mean values were 1.59 to 3.30 mgL^{-1} and 2.47 ± 0.28 mgL^{-1} respectively. There was no significant difference ($p \geq 0.05$) between the seasonal mean values. Sodium ion range and mean value were 0.10 to 3.45 mgL^{-1} and 1.98 ± 1.23 mgL^{-1}. Sodium in the rainy season comprised a range from 0.10 to 2.77 mgL^{-1} with a mean value of 1.41 ± 0.57 mgL^{-1} whilst the dry season value was 1.70 to 3.45 mgL^{-1} and 2.54 ± 0.31 mgL^{-1}. The dry season mean value was higher than the rainy season with no significant difference ($p \geq 0.05$) between the two seasonal mean values (Table 4 and Figure 3). The sulphate overall range and mean value was 0.47 to 54.54 mgL^{-1} and 17.06 ± 4.98 mgL^{-1} respectively (Table 1). The value during the rainy season had a range and mean values from 4.07 to 19.38 mgL^{-1} and 12.79 ± 2.85 mgL^{-1} whilst the dry season range and mean values were 0.47 to 54.54 mgL^{-1} and 21.33 ± 9.68 mgL^{-1}. The dry season value was higher than the rainy season value. Sulphate showed no significant difference ($p \geq 0.05$) between the two seasonal mean values (Table 4 and Figure 3). Chloride ion ranged from 1.44 to 16.28 mgL^{-1} and had a mean value of 9.71 ± 4.09 mgL^{-1}. The chloride range and mean values for dry season were 6.91 to 16.28 mgL^{-1} and 11.34 ± 1.42 mgL^{-1} respectively while the values for rainy season was 1.44 to 13.94 mgL^{-1} and 8.08 ± 1.76 mgL^{-1} (Table 4 and Figure3). The range and mean values of bicarbonate ranged from 48.00 to 120.00 mgL^{-1} and 87.00 ± 7.24 mgL^{-1} respectively while hardness range and mean values were 46.05 to 68.03 $mgCaCO_3L^{-1}$ and 58.03 ± 7.15 $mgCaCO_3L^{-1}$ respectively (Table 1). The rainy season range and mean values of bicarbonate in water source were 48.00 to 86.40 mgL^{-1} and 66.00 ± 5.90 mgL^{-1} whilst the dry season value was 93.60 to 120.00 mgL^{-1} and 108.00 ± 4.38 mgL^{-1}. There was a very highly significant difference observed over the mean value of the dry season (Table 4 and Figure3). The chemical concentrations in the river were all lower in the rainy season compared to the dry season; this was probably due to the High volume of water from rainfall and the flow rate velocity, which resulted in the dilution of the chemical ions. On the other hand, rock weathering and effect of evaporation must have contributed to the higher values observed in the dry season. It can therefore be inferred from the ternary plot that rock weathering and evaporation of carbonate and calc-silicate rocks [33] controlled the major ion contribution in the river water. The range and mean values of hardness were 47.11 to 64.67 $mgCaCO_3L^{-1}$ and 55.59 ± 2.52 $mgCaCO_3L^{-1}$ in the rainy season whilst the dry season values were 46.05 to 68.03 $mgCaCO_3L^{-1}$ and 60.46 ± 3.17 $mgCaCO_3L^{-1}$. Hardness showed no significant difference ($p \geq 0.05$) between the two seasonal mean values (Table 4 and Figure3). The hardness concentrations were generally low, and according to [34] on the classification of mineral water, the water type was soft fresh water type with values recorded below the recommended drinking water standard. The ionic order of dominance was $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$; $HCO^{3-} > Cl^{-} > SO_4^{2-}$.

Heavy metal parameters of surface water quality

The overall iron concentration values ranged from 0.34 to 1.66 mgL^{-1}Fe with a mean value of 0.81 ± 0.13 mgL^{-1}Fe (Table 1). WHO detected Fe in all the water samples at concentrations above the permissible limit for drinking water? The order of dominance in the dry season was Fe > Zn > Ni > Cr > Cd > Pb while the order in the rainy season was Fe > Zn > Cr > Ni > Cd > Pb. The rainy season range and mean values of iron were 0.47 to 0.88 mgL^{-1}Fe and 0.68 ± 0.08 mgL^{-1}Fe while the dry season values were 0.34 to 1.66 mgL^{-1}Fe and 0.94 ± 0.25 mgL^{-1}Fe respectively. Iron value in the dry season was higher than in the rainy season (Table 5 and Figure4). Zinc concentration ranged from 0.08 to 0.43 mgL^{-1} with a mean value of 0.26 ± 0.04 mgL^{-1}. The dry and rainy season range and mean values of Zn were 0.08 to 0.38 mgL^{-1} and 0.23 ± 0.13 mgL^{-1}; 0.13 to 0.43 mgL^{-1} and 0.29 ± 0.06 mgL^{-1} respectively (Table 5 and Figure4). The rainy season value was higher than the dry season value. All samples occurred within the permissible limit for drinking water. Zn is needed for normal body growth and function but at too low a concentration, there could be damage to gastrointestinal, reproductive organs and the central nervous system [35]. The range and mean values of cadmium were 0.00 to 0.03 mgL^{-1} and 0.02 ± 0.00 mgL^{-1} respectively. In the dry season, the value of cadmium ranged from 0.01 to 0.03 mgL^{-1} with a mean value of 0.02 ± 0.00 mgL^{-1} while the rainy season range and mean values were 0.00 to 0.03 mgL^{-1} and 0.02 ± 0.00 mgL^{-1} respectively (Table 5). Concentration was similar across the seasons with 92% of the samples exceeding the recommended limit by NSDWQ and showed no regular pattern. The high concentration may be linked to the geology of the area, as cadmium is rich in feldspar minerals [23, 9]. Other possible suspected source includes emission from diesel-powered engine used in oil palm production, which is a common vocation in the study area [36]. Cadmium toxicity in the body causes bone, liver and kidney damage. The concentration of chromium in water ranged from 0.06 to 0.26 mgL^{-1} with a mean value of 0.14 ± 0.02 mgL^{-1} (Table 1). The range and mean values of chromium during the rainy and dry seasons were 0.06 to 0.26 mgL^{-1} and 0.15 ± 0.04 mgL^{-1}; 0.08 to 0.17 mgL^{-1} and 0.12 ± 0.02 mgL^{-1} respectively. The rainy season value was higher than the dry season. The mean values showed no significant difference ($p \geq 0.05$) between the seasons (Table 5 and Figure4).

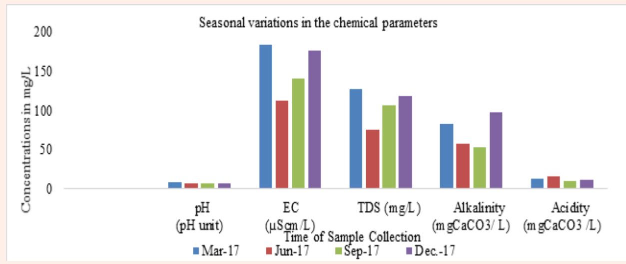

Figure 2: Showing the Seasonal variation in the chemical concentrations of water quality.

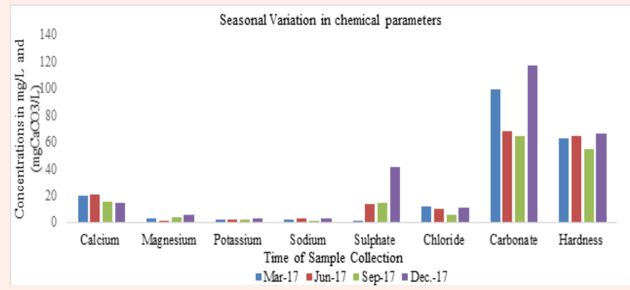

Figure 3: Showing the seasonal variations in the ion concentrations of water quality

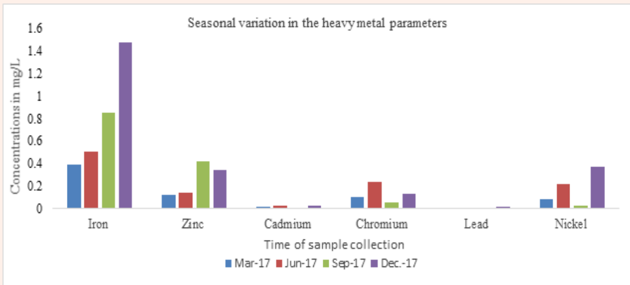

Figure 4: Showing the seasonal variations in the heavy metal concentration of water quality

Lead and nickel concentrations ranged in values from 0.00 to 0.02 mgL^{-1} and 0.02 to 0.41 mgL^{-1} with mean values of 0.01 ± 0.00 mgL^{-1} and 0.18 ± 0.04 mgL^{-1} respectively (Table 1). The rainy season value of nickel was 0.02 to 0.26 mgL^{-1} with a mean value of 0.13 ± 0.04 mgL^{-1} while the dry season range and mean values were 0.06 to 0.41 mgL^{-1} and 0.23 ± 0.07 mgL^{-1}. The dry season mean value was higher than the rainy season. The mean values of the two seasons showed no significant difference ($p \geq 0.05$). Lead concentration in the study area had 17% of the samples above the permissible limit for drinking water and was attributed majorly to domestic sources such as, burning of agricultural waste, vehicular fumes, and fumes from diesel powered plants [9]. Lead is a toxic metal that can bio-accumulate in the body over time and affect body processes. Children are easily affected by lead poisoning causing a brain disease. Lead toxicity may weaken renal function, reduce the quality of red blood cell production, reduce the effectiveness of the nervous system and cause blindness [4]. The order of dominance was Fe > Zn > Ni > Cr > Cd > Pb. The works of [37] suggested that low coefficient of variation (< 10%) indicates low degrees of anthropogenic contribution while on the other hand; a high coefficient of variation (90%) indicates a high degree of anthropogenic situation. However, in this present study the percentage coefficient of variation (% CV) of Fe, Zn, Ni, Cr, Cd, and Pb were 56.69, 53.33, 80.65, 52.85, 55.16 and 86.15 respectively. This implies that most of the heavy metals have been affected by human activities to moderate degrees. Nickel and Lead had a high degree of anthropogenic contribution.

Nutrient compound contents of water quality

Nutrient enrichment in the river was associated with mineralization of nitrate and phosphate, which was possibly caused from surface runoffs and processes existing from immediate environment such as leaching from farmland, soil erosion, surface runoff, and dumping of waste [38]. Nitrate overall concentration value ranged from 0.02 to 1.60 mgL^{-1} with a mean value of 0.41 ± 0.14 mgL^{-1} while phosphate ion range and mean values were 0.23 to 17.80 mgL^{-1} and 6.13 ± 1.87 mgL^{-1} respectively (Table 1). Silica and organic matter concentrations ranged from 0.08 to 1.60 mgL^{-1} and 0.45 to 14.72 mgL^{-1} respectively with mean values of 0.54 ± 0.12 mgL^{-1} and 6.01 ± 1.55 mgL^{-1} (Table 1). The dry season range and mean of nitrate were 0.13 to 1.60 mgL^{-1} and 0.75 ± 0.21 mgL^{-1} while the rainy season values were 0.02 to 0.10 mgL^{-1} and 0.07 ± 0.02 mgL^{-1} (Table 6 and Figure 5). The dry season mean value was higher than the rainy season value. Generally, the nitrogen content was low across the seasons. There was a significant seasonal difference ($p < 0.05$) in the mean values between the two seasons (Table 6). The effect of dilution from rainfall may have accounted for the very low concentration during the rainy season. Phosphate had a range and mean value in the rainy season from 0.23 to 12.40 mgL^{-1} and 6.99 ± 2.44 mgL^{-1} respectively. Although, the value was higher than the corresponding values for the dry season (0.35 to 17.80 mgL^{-1} and 5.28 ± 3.03 mgL^{-1}) the mean values were not statistically different ($p \geq 0.05$) over the two seasons. The phosphate concentration exceeded 5 mgL^{-1} guideline set by the [39] Federal Environmental Protection Agency. The high concentration of phosphate could be attributed to several washings with phosphate rich soaps in and around the riverbank as well as the effect of phosphate rich fertilizers from nearby farmlands, which were washed by surface runoff into the river. Silica concentration in the dry season had a range and mean values from 0.26 to 1.60 mgL^{-1} and 0.71 ± 0.21 mgL^{-1} while the rainy season values were 0.08 to 0.75 mgL^{-1} and 0.38 ± 0.10 mgL^{-1} respectively (Table 6 and Figure5). The dry season value was higher than the rainy season value but there was no significant seasonal difference ($p \geq 0.05$) in the mean values. For organic matter concentration during the dry season, the range and mean values were 0.45 to 14.72 and 4.51 ± 2.30 mgL^{-1} while the rainy season values were 1.88 to 13.24 mgL^{-1} and 7.51 ± 2.09 mgL^{-1} respectively. The rainy season mean value was higher than the dry season possibly due to rainfall, and surface run offs that washed different organic substances into the river and caused an increase in concentration. There was no significant difference ($p \geq 0.05$) over the two mean seasonal values (Table 6 and Figure 5).

Oxygen contents of water quality

Dissolved oxygen is one of the most important indicators of water quality. It is temperature dependent on the amount of oxygen available in the surrounding air and the atmospheric pressure [40]. The lower the DO, the more stressed the water is. The overall dissolved oxygen and dissolved oxygen saturation values ranged from 0.95 to 8.80 mgL^{-1} and 11.38 to 113.99 mgL^{-1} respectively with mean values of 5.14 ± 0.76 mgL^{-1} and 64.40 ± 9.49 mgL^{-1} (Table 1). The lowest value was recorded at station B however, DO was generally low across the stations. The dissolved oxygen value in the dry season ranged from 4.00 to 7.60 mgL^{-1} and 5.77 ± 0.57 mgL^{-1} while the rainy season values were 0.95 to 8.80 mgL^{-1} and 4.52 ± 1.44 mgL^{-1} respectively. The dry season mean value was higher than the rainy season value but there was no significant difference ($p \geq 0.05$) between the two seasons (Table 6 and Figure 6). The average DO of 5.14 mgL^{-1} will support fish farming, and this was similar to the findings of [41] who reported 4 - 9 mgL^{-1} of DO is the optimal range that will support large and diverse fish population. DO saturation range and mean values in the dry season were 53.19 to 92.68 mgL^{-1} and 72.08 ± 5.79 mgL^{-1}, while the values were 11.30 to 113.99 mgL^{-1} and 56.72± 18.41 mgL^{-1} in the rainy season (Table 6 and Figure6). The dry season values were higher than the rainy season values ($p \geq 0.05$). The BOD and COD range values were from 1.20 to 6.40 mgL^{-1} and 0.00 to 50.29 mgL^{-1} with mean values of 3.35 ± 0.41 mgL^{-1} and 17.17 ± 3.88 mgL^{-1} respectively (Table 1). According to the work of [42] cited [43] who reported that BOD of unpolluted waters is less than 1.00 mg/L; moderately polluted (BOD 2.0 - 9.0 mg/L) while heavily polluted waters have BOD more than 10.0 mg/L which also agrees with the works of [44]. The average BOD value therefore suggests the river was moderately polluted. In the rainy season, BOD concentration ranged from 1.20 to 6.40 mgL^{-1} with a mean value of 3.44 ± 0.81 mgL^{-1} while the range value of 2.40 to 19.60 mgL^{-1} with a mean value of 3.27 ± 0.28 mgL^{-1} in the dry season (Table 6 and Fig.6). The rainy season values were slightly higher than the dry season values but not statistically different ($p \geq 0.05$) in mean values. In the dry season, the range and mean values of COD was 0.00 to 50.29 mgL^{-1} and 21.10 ± 7.30 mgL^{-1} while the rainy season range and mean values were 5.00 to 20.49 mgL^{-1} and 13.24 ± 2.60 mgL^{-1}. The dry season value was slightly higher than the rainy season value Table 7.

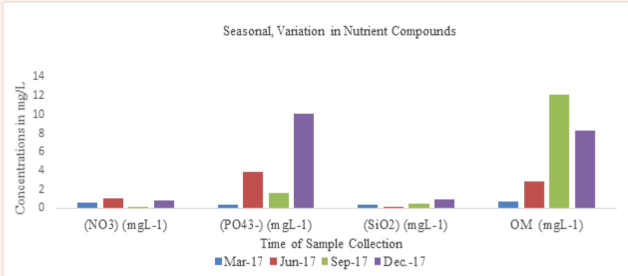

Figure 5: Showing the seasonal variations in nutrient compounds of water quality.

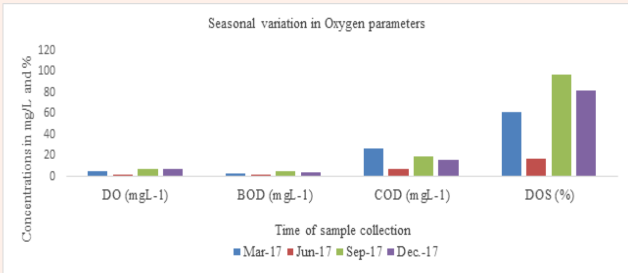

Figure 6: Showing the seasonal variations in oxygen concentrations of water quality.

Conclusion

The heavy metal concentrations were found to exceed the permissible limits in all except for Zinc. Apparent colour, true colour, turbidity, Phosphate, BOD, Fe, Cr, Cd, Pb, and Ni, had high concentrations above drinking water standard and could be of concern as these exceeded the recommended permissible limit for drinking water by [30, 31, 40]. The remaining parameters (air and water temperature, TDS, conductivity, Ca^{2+}, Mg^{2+}, N^{+}, K^{+}, Cl^{-}, SO_4^{2-} , HCO_3^{-}, Zn, pH, alkalinity, acidity, NO_3^{-}, PO_4^{3-}, SiO_2, OM, DO, COD, DO saturation) had low concentrations and were within the standards for drinking water and therefore not in concentration harmful to human health. It can be concluded from the present study that the Shasha river water quality in terms of its physico-chemical parameters were not above the permissible limits set by WHO and NSDWQ except for colour turbidity and Phosphate. Whereas, the heavy metal levels suggest a significant health risk given the toxicity of these metals. Therefore, the water is not suitable for drinking and would need some treatment to be carried out to make the water completely fit for drinking.

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