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Spatial and temporal variation of physicochemical parameters and heavy metals in textile polluted 'Iya-Alaro' River, Lagos, Nigeria

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Abstract

Spatial and temporal variations of physicochemical parameters and heavy metals was assessed from a textile-polluted River in Lagos state. Sample stations were selected based on proximity to the textile industries and referenced as upper stream (SS1), Mid-stream (SS2), and Downstream (SS3). Eleven (11) physicochemical parameters and six (6) heavy metals were determined from water samples and sediment which were monitored bi-monthly from January to November; 2020 using standard methods according to APHA. Mean monthly value for Carbondioxide was 66.7±10.04 - 379.4±142.5mg/l, Total hardness ranged from 38.17±2.3 – 69.2± 4.4, Salinity from 0.18±0.02 - 1.09±0.13, Temperature from 25.3±0.44 - 27.87±0.2°C, Conductivity ranged from 477.6±28.6 – 1030.7±17.0 µS/cm, DO ranged from 0.2±0.04 – 3.7±0.91mg/L, pH ranged from 6.53±0.3 – 7.38±0.2, nitrate from 0.6±0.3 – 11.07±1.4mg/L, nitrite from 0.0 – 0.61±0.12mg/l, alkalinity from 206.5±36.3 – 287.5±0.6 and phosphate from 1.53±0.5 – 2.12±1. Heavy metals results revealed significant spatial variations: Iron (Fe) ranged from 3.78±0.52 – 5.79±1.78; Copper ranged from 0.65±0.5 – 1.12±0.6; Zinc ranged from 7.14±7.03 – 9.07±9.24; Manganese ranged from 4.49±5.74 – 7.7±10.57; Lead (Pb) ranged from 0.03±0.02 – 0.06±0.01 and Cadmium ranged from 0.12±0.13 – 0.22±0.27mg/L. Significant temporal differences were observed between wet and dry seasons during the study ($P \leq 0.05$). The spatial Pollution level of the three sampling stations follows the sequence, station 1>2>3. A comparison of the measured parameters with the World Health Organization (WHO) indicates that the river has been significantly polluted and is not suitable for the growth and survival of fish species. It is recommended that government and non-governmental organization should support further research in the study area.

Keywords: Physicochemical parameters, Heavy metals, Textile effluent, Water and sediment samples

Introduction

The textile industry is the second high pollution-producing industry in Lagos state asides from chemical and pharmaceutical industries with respect to the release of toxic chemicals into the environment according to an analysis conducted by Oketola and Osinbajo (2009). Textile industries typically discharge large amount of highly concentrated toxins into the environment (Holkar, et al and Pandit, 2016, Jegatheesan, et. al 2016). Depending on the end products, textile effluent may have extreme concentrations of pH, temperature, heavy metals, colour, morbidity, sodium chloride, solvent etc (FEPA 1999; Holkar et. al 2016; Jegatheesan, et. al 2016). Due to the high flow of wastewater, most textile manufacturing companies discharge their waste into nearby water bodies where the toxins can potentially and adversely affect aquatic life, fresh water supplies and public health. Rapid industrialisation, urbanization and population increase in the last few decades caused a dramatic increase in the demand for river water and significant deterioration in water and sediment quality especially near large industrial complexes and in the lower basin. These trends are expected to be continued, unless appropriate management strategies are carried out to ensure adequate water supplies and to restore water and sediments qualities to appropriate standards for the intended uses (Chun et al. 2001; Venkatramanan et al. 2014).

This research evaluates the physicochemical parameters of the textile polluted river popularly known as the 'Iya-Alaro' River and selected heavy metals in water and surface sediments. Over the years, people inhabiting the environment have tended to believe that the river is a supernatural one, and therefore, they tend to worship and give sacrifice offerings to the river. Reasons have been known to them that it changes colours as it pleases over a certain period of time. Also, during the rainy season, it becomes dangerous. Although, the colour changes are a result of the textile effluent of different industries being discharged into the river. The inhabitants of that area use the water for their domestic purposes. The significance of water on human health cannot be over emphasized. Therefore, this study assessed the quality of wastewater emanating from various industries especially textile manufacturing industries in the study area, and its potential impact on the aquatic environment and public health. This study will also provide data for more future work on the river.

Moreover, the biotic component of the aquatic ecosystem, which consists of fauna and flora, are indispensable economic resources. Major components of aquatic fauna are the finfish and shellfish (shrimps, prawns, crabs, lobsters, clams, scallops, periwinkles and oysters among others). Rural artisans who depend on fisheries as a means of livelihood concentrate on shallow water bodies like rivers, creeks, lakes and lagoons for their fishing expedition; this is due to their inability to explore larger water bodies because of limited capital. In Nigeria, the artisanal fisheries sector produces bulk of fish consumed by the populace; in addition, this fisheries sector provides income, employment, raw materials and foreign exchange to the Nigerian populace and the nation (Kumolu-Johnson, 2004). However, in recent times, Nigeria inland water bodies have been subjected to various forms of degradation due to pollution arising from domestic wastes, industrial effluent, agricultural run-offs, oil spillage, mine effluents and obnoxious fishing practices (Ndimele, 2008). The result is that the associated fishery, the biota and the ecosystem upon which fishers depend for a living are destroyed and consumption of fish caught from such polluted water bodies pose severe danger to the consumers (Kumolu-Johnson et al., 2005). One of such pollutants is heavy metals.

Heavy metals are pollutants that have been a source of concern for aquatic ecologists because most of them are non-biodegradable; once they enter the system of a biota, they persist there and bio-accumulate along the food chain (Ndimele et al., 2009). The presence of heavy metals in aquatic ecosystems is the result of two main sources of contamination; natural processes or natural occurring deposits and anthropogenic activities. Heavy metals are the most common environmental pollutants and a serious threat due to their toxicity, long persistence, biomagnification and bioaccumulation in the food chain. Heavy metals from natural and anthropogenic sources such as industrial effluents, agricultural run-off, transport, burning of fossil fuel, geochemical structures and mining activities are continually released into aquatic ecosystems. The toxic effects of the metals depend on the metal properties. In the fresh water environment, toxic metals are potentially accumulated in water, sediments and aquatic organisms and are subsequently transferred to man through the consumption of these aquatic organisms and from consumption of water from these aquatic bodies. Studies on heavy metals in rivers, lakes, fish and sediments have been a major environmental focus especially during the last decade (Fernandes et al., 2008; Pote, et al., 2008; Praveena, et al., 2008). Sediments have been reported to form the major repository of heavy metals in the aquatic ecosystem while both allochthonous and autochthonous influences could make a concentration of heavy metals in the water high enough to be of biological significance (Oyewo and Don-Pedro, 2003). Water is commonly employed as a pollution indicator by heavy metals and sediments can provide a deeper insight into the long-term pollution state of the water body (Ikem, et al., 2003). Heavy metal content in rivers may vary between the water column and the bed sediments. However, variation in concentration of parameters depends on concentration from processes operating within the catchments. Some heavy metals that were checked for in the water and sediments include Manganese (Mn), Copper (Cu), Zinc (Zn), Iron (Fe), Cadmium (Cd) and Lead (Pb).

The aim of this study is to investigate and determine the physico-chemical parameters and concentration of selected heavy metals in the water and sediment of Iya-Alaro. This would be achieved by the: determination of the physico-chemical parameters of the water body from three (3) sample stations; determination of the heavy metal concentration in water and sediments of the selected sampling stations; inferring if the water from the river is safe for the sustenance of the aquatic organisms inhabiting the biota when compared against set standards by World Health Organization (WHO); determination of the effect of textile influent on the marine environment.

Materials and Methods

Study Area

The study area is located in the Ojota area of Lagos, Nigeria and lies approximately between longitude 2o42'E and 3o42'E and latitude 6o22'N 6o52'. It flows through a series of textile industries from the Alade market to under the Ojota bridge and discharges into the Lagos lagoon. This study is geared toward determining the physicochemical parameters and concentration of heavy metals in the water and bottom sediments from Iya-alaro river, Ojota, Lagos State, Nigeria, with a view to establishing basic data on the current pollution status of the river. The results obtained from this study would also provide information on current levels of metals in the water and sediments of the river, contributing to the effective monitoring of both environmental quality and the health of the organisms inhabiting the river. The samples of this study were obtained from station 1, which is the upper stream (Alade market) and station 2, which is the midstream (Iya Alaro River), and station 3 which is the downstream (Iya Alaro River) in which textile effluent and waste of other industries are being discharged into.

Collection of Samples:

Water and sediment samples for the determination of physicochemical parameters and heavy metal analysis were collected once in two months for 12 months (January – November; 2021). These were collected in 2-liter (screwed cap) plastic bottles that has been previously rinsed with 10% nitric acid for 48 hours and rinsed with distilled water. The water samples were stored immediately after collection in a cooler to ensure that the physical and chemical properties of the samples were retained. Sediment samples were collected from the river and were immediately transferred into polypropylene bags and transported to the laboratory. The temperature was measured in situ with a mercury-in-glass thermometer. Carbon dioxide, total alkalinity, and total hardness were determined by titration.

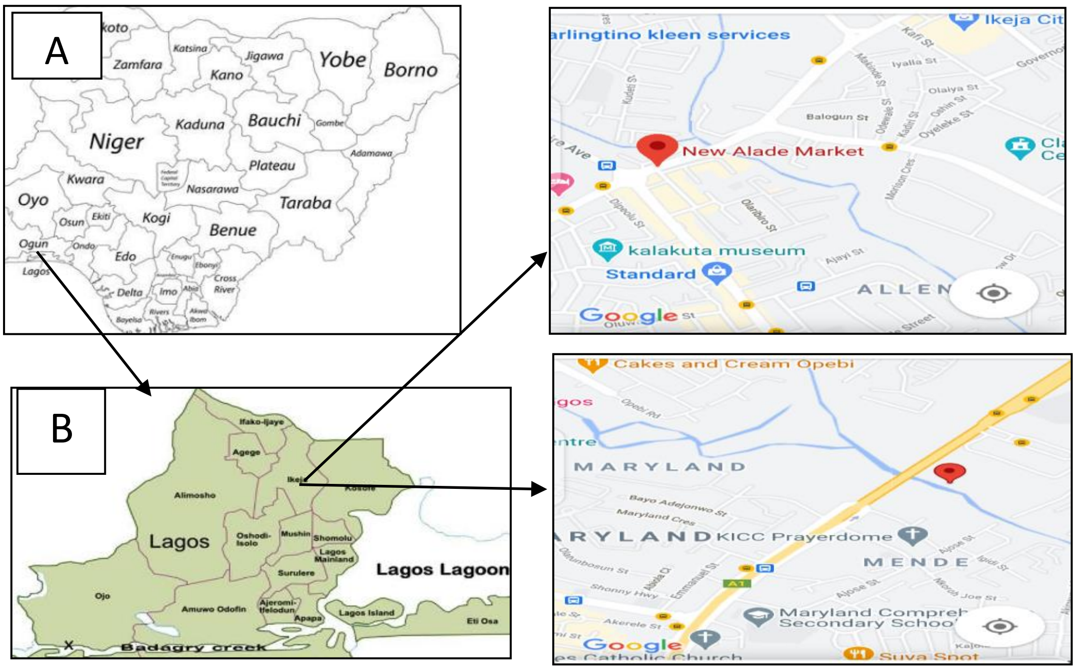

Figure 1: Map of the study area: A is the map of Nigeria, B is the map of Lagos state inset the sampling station 1 (Alade market area of the river), SS2 Mid- stream) and SS3 (Lower-stream) of the Iya-Alaro river, Ikeja-Lagos, Nigeria.



Laboratory Analysis

Analysis of Physicochemical characteristics was carried out using standard methods as prescribed by APHA (1995) and ASTM (2003) on the following: Temperature (^{0}C), pH, Conductivity (µS/cm), salinity (‰), total alkalinity (mg/l), carbondioxide (mg/l). Total hardness (mg/l), dissolved oxygen (mg/l), phosphate (mg/l), nitrate (mg/l), and nitrite (mg/l).

The metals of concern in the investigation are Lead (Pb), Cadmium (Cd), Copper (Cu) Zinc (Zn), Manganese, and iron (Fe). The metals were determined on a filtrate of samples digested by atomic absorption spectrometry. Test results were validated with calibration curves obtained with certified metals standards.

Statistical Analysis

Statistical analysis procedures provide knowledge and assist the interpretation of environmental data (Sena, et al., 2002) and a wide variety of these have now been in use due to the increasing number of physicochemical parameters and heavy metals status in the river. The result of this study was analysed statistically using the Excel program and Statistical Package for Social Science (SPSS). The Excel program was used to analyse minimum concentration (min), maximum concentration (max), average concentration, and standard deviation (SD). The correlation matrix and graph were analysed using the SPSS. The probability values of $p<0.05$ was used as statistically significant and not significant respectively.

Results

Temporal Variation of Physicochemical Parameters and Heavy metals

The results of the physical and chemical parameters quantified from the analysis of water samples as presented in table 1, shows the mean monthly variations in the study area within the period of study (January – November; 2020). Dissolved oxygen was significantly different from one month to another throughout the period of study with the highest values of 3.7±0.91mg/l in March (2019) and the lowest of 0.2±0.04mg/l in September (2020). Carbondioxide ranged from 66.7±10.04 in March to 379.4±142.5mg/l in January. Carbondioxide was the most varied water quality parameter in the study area. Total hardness ranged from 38.2±5.9mg/l in November to 69.2±4.4mg/l in September. Salinity ranged from 0.18±0.02‰ to 0.58±0.04‰. Temperature also varied significantly from 25.3±0.44°C in November to 27.87±0.2°C in January. The values for Conductivity varied throughout the study period with a minimum of 477.6±28.6uS/cm in November to a maximum of 1030.7±17.0uS/cm in January. Nitrate and nitrite also varied significantly from 0.6±0.3mg/l in March to 11.07±1.4mg/l in November and 0.00+0.0mg/l in November to 0.67±0.14mg/l in May respectively. However, alkalinity varied slightly from 206.5±36.3mg/l in May to 287.5±0.6 in January. Phosphate was steady throughout the study period between 1.53±0.5 in March to 2.12±41.0 in September. The graphical representations for all the water quality parameters are shown in figure 2.

Table 1: Mean temporal variations of physicochemical parameters from three (3) Sample stations in Industrially polluted (Iya-Alaro) river, Lagos

Parameters	January	March	May	July	September	November
Diss. Oxygen	1.4±0.4 [a]	3.7±0.91 [b]	0.2±0.1 [c]	1.9±0.3 [a]	0.2±0.04 [c]	0.2±0.12 [c]
Carbondioxide	66.7±10.4 [a]	7.8±3.21 [b]	379.4±142.5 [c]	376.5±49.5 [c]	221.3±23.8 [d]	106.3±29.8 [e]
Total Hardness	38.17±2.3 [a]	40.56±5.4 [a]	45.6±9.4 [b]	48.6±8.56 [b]	69.2±4.4 [c]	38.2±5.9 [a]
Salinity	1.09±0.13 [a]	0.18±0.02 [b]	0.53±0.23 [b]	0.49±0.2 [b]	0.58±0.04 [b]	0.34±0.02 [b]
Temperature	27.87±0.2 [a]	27.3±0.6 [a]	25.50±0.4 [b]	26.2±0.7 [c]	26.4±0.4 [c]	25.3±0.44 [b]
Conductivity	1030.7±17.0 [a]	943.6±39.3 [b]	669.3±33.6 [c]	809.9±34.5 [b]	544.5±131.9 [d]	477.6±28.6 [d]
Ph	7.37±0.1 [a]	7.38±0.2 [a]	6.53±0.3 [b]	7.35±0.13 [a]	7.10±0.17 [a]	6.83±0.03 [b]
Nitrate	0.88±0.12 [a]	0.60±0.3 [a]	3.26±1.46 [b]	2.60±1.0 [c]	8.08±0.22 [d]	11.07±1.4 [e]
Nitrite	0.38±0.2 [a]	0.05±0.02 [b]	0.67±0.14 [c]	0.61±0.12 [c]	0.08±0.01 [b]	0.00±0.0 [d]
Alkalinity	287.5±0.6 [a]	275.23±0.8 [a]	269.07±69.9 [a]	270.3±60.9 [a]	253.7±27.8 [b]	206.5±36.3 [c]
Phosphate	1.60±0.53 [a]	1.53±0.5 [a]	1.54±0.29 [a]	1.73±0.1 [a]	2.12±41.1 [a]	1.86±0.24 [a]
Iron	6.27±1.6 [a]	0.2±0.04 [b]	0.2±0.04 [b]	1.07±0.42 [c]	1.45±0.4 [c]	1.78±0.69 [d]
Copper	0.04±0.01 [a]	0.01±0.06 [a]	0.01±0.01 [a]	0.01±0.01 [a]	0.02±0.01 [a]	0.03±0.01 [a]
Zinc	0.42±0.12 [a]	1.23±0.23 [b]	1.23±0.23 [b]	1.29±0.29 [b]	2.34±0.27 [c]	2.21±0.56 [c]
Manganese	0.01±0.01 [a]	0.09±0.06 [b]	0.10±0.6 [a]	0.08±0.07 [b]	0.3±0.07 [c]	0.42±0.06 [d]
Lead	0.03±0.01 [a]	0.02±0.01 [a]	0.02±0.01 [a]	0.02±0.01 [a]	0.03±0.02 [a]	0.01±0.02 [a]
Cadmium	0.01±0.02 [a]	0.004±0.02 [b]	0.04±0.02 [a]	0.01±0.01 [a]	0.04±0.01 [a]	0.02±0.01 [a]

Spatial Variation of Physicochemical Parameters and Heavy Metals in Dry and Wet seasons from Iya-Alaro River, Lagos compared with WHO limits

The results of the spatial variation of physicochemical parameters and heavy metals in the dry and wet seasons from Iya-Alaro River is shown in table 2. The mean temperature from the three sample stations for the dry season (26.8^{0}C) and wet season (26.0^{0}C) are similar but slightly lower in wet season, this is above the WHO limit (25^{0}C). Alkalinity was 256.3 in dry season and 243.4 in wet season. Mean dissolved oxygen for dry season (1.75mg/l), and wet (0.73mg/l) which is far below the WHO standard (5.0mg/l); carbondioxide for dry season (145.0mg/l) and wet (234.6mg/l) were observed to be in excess of the WHO limit (10mg/l); Salinity for dry season (0.6‰) and wet season (0.47‰); pH for dry season was 6.95 and wet season 7.02; nitrite nitrate and phosphate for dry season were 0.37, 1.6 and 1.5mg/l, and were 0.28, 7.26 and 1.9mg/l for wet season respectively. Mean values of total hardness and conductivity for dry season were 41.9mg/l and 881.2µS/cm. While for wet season are 52.0mg/l and 610.6 µS/cm. Heavy metals in dry and wet season from the three sample stations showed significant variations as follows: Iron (fe) was 2.97 and 1.43mg/l which is above WHO limit (0.3mg/l); copper (Cu) was 0.03 and 0.01mg/l; zinc (Zn) was 0.73 and 1.94mg/l far above the required limit (0.2); manganese was 0.09 and 0.25mg/l; lead (Pb) was 0.02 and 0.02mg/l and cadmium (Cd) was 0.01 and 0.02mg/l respectively.

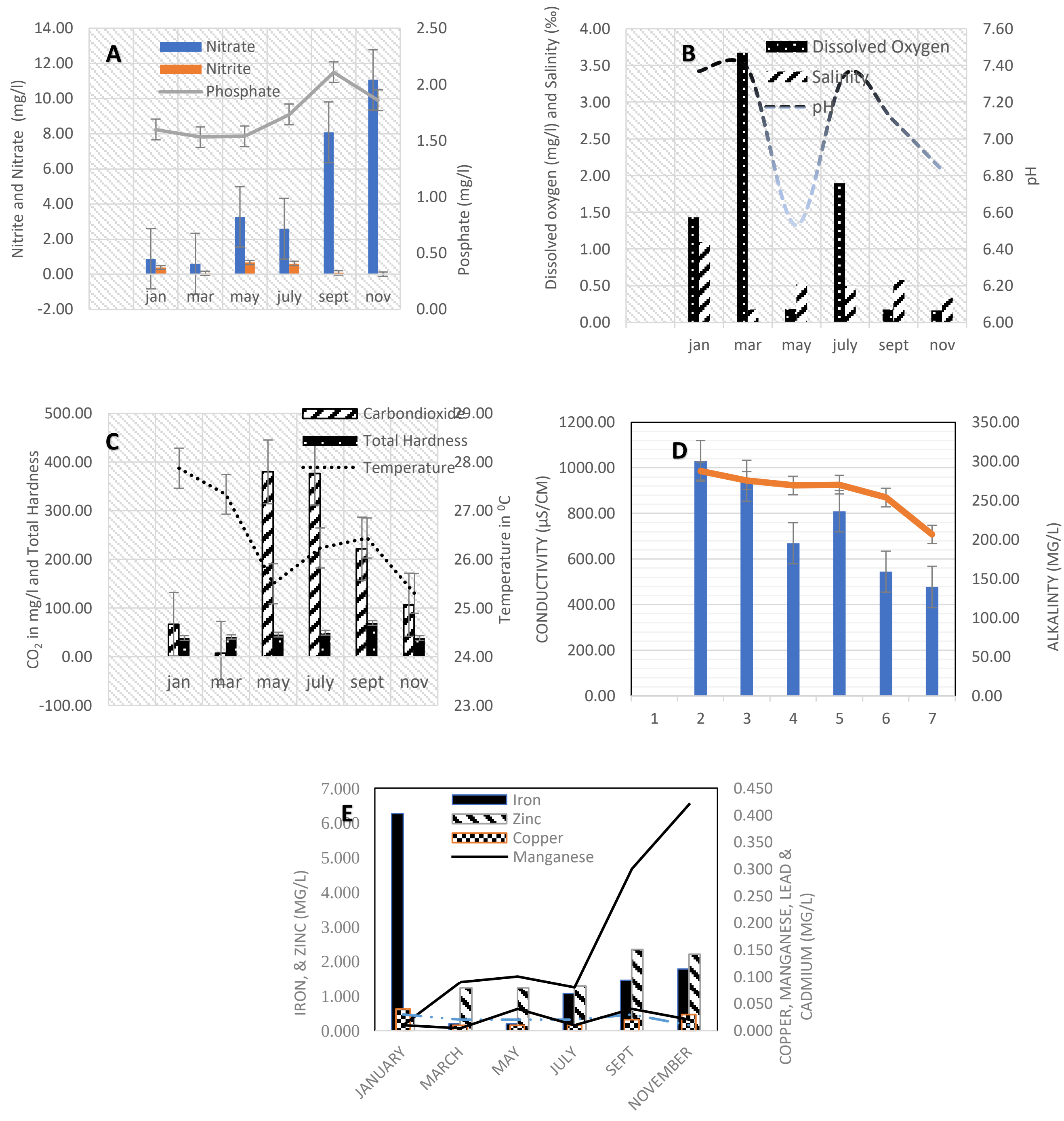

Figure 2: Graphs showing mean temporal variations of Physicochemical parameters and Heavy metals (**A**) Dissolved oxygen, salinity & PH (**B**) Carbondioxide total hardness & temperature (**C**) Nitrate, nitrite & phosphate (**D**) Conductivity & alkalinity (**E**) Iron, zinc, copper & manganese in textile polluted river (Iya-alaro), Lagos, Nigeria.

Table 2: Spatial Variation of Physicochemical Parameters and Heavy Metals Analysis in samples stations, At Iya-Alaro River, Lagos.

Physicochemical Parameters/ Metals	**Dry Season**			**Wet Season**			**WHO**
	SS1	SS2	SS3	SS1	SS2	SS3	Limits
Temperature	26.6±1.3	26.8±0.9	27.1±1.6	25.5±0.5	26.5±0.6	26.1±0.8	25
Alkalinity	366.3±32.2	225.4±36.4	177.2±30.5	279.8±33.2	248.8±48.8	201.6±30.4	120
Dissolved Oxygen	1.3±1.4	1.7±1.7	2.25±2.2	0.62±0.8	0.79±0.9	0.8±5.0	5.0
Carbondioxide	196.5±28.1	133.6±21.9	105.1±11.6	295.6±18.9	240.7±14.7	167.7±7.8	<10
Salinity	0.71±0.5	0.6±0.5	0.47±0.4	0.54±0.19	0.5±0.12	0.37±0.2	0-40
Ph	7.14±0.6	6.9±0.6	6.83±0.5	7.05±0.2	7.1±0.36	6.93±0.6	6.5-8.5
Nitrite (mg/l)	0.47±0.4	0.37±0.3	0.27±0.2	0.26±0.4	0.25±0.4	0.34±0.3	<1.0
Nitrate (mg/l)	2.07±1.9	1.75±1.8	0.93±0.6	8.11±4.5	7.26±4.1	6.43±4.4	50
Phosphate	1.27±0.5	1.6±0.1	1.51±0.4	2.13±0.4	1.81±0.2	1.76±0.1	2.0
Total hardness	49.3±8.1	41.7±3.1	34.8±3.9	51.4±17.2	52.03±15.8	52.6±18.2	40-400
Conductivity	1204.6±16.1	824.8±20.1	614.3±25.6	755.3±34.8	599.0±22.6	477.7±30.1	500
Iron	3.85±3.8	2.7±3.2	2.36±2.1	1.47±0.4	1.49±0.8	1.34±0.6	0.3
Copper	0.03±0.02	0.02±0.1	0.04±0.1	0.02±0.01	0.02±0.01	0.01±0.01	0.5
Zinc	0.96±0.5	0.7±0.4	0.55±0.4	2.36±0.6	1.82±0.5	1.66±0.6	0.2
Manganese	0.14±0.12	0.07±0.1	0.06±0.1	0.29±0.12	0.27±0.2	0.19±0.2	0.5
Lead	0.04±0.02	0.02±0.1	0.02±0.1	0.03±0.02	0.02±0.1	0.01±0.1	0.01
Cadmium	0.01±0.01	0.01±0.1	0.01±0.1	0.03±0.02	0.02±0.1	0.01±0.1	0.01

Table 3: The Correlation coefficients among Water Physocochemical parameters and Heavy-metals from three (3) sampling stations from Iya-alaro river, Ikeja, Lagos.

Parameters	DO	CO_2	TH	Sal	Temp	Cond.	pH	NO_3	NO^{-1}	Alk	Ph	Fe	Cu	Zn	Mn	Pb	Cd
D. Oxygen	1																
Carbondioxide	-0.43	1															
T. Hardness	-0.35	0.39	1														
Salinity	-0.28	0.01	0.02	1													
Temperature	0.64	-0.57	-0.12	0.46	1												
Conductivity	0.75	-0.32	-0.43	0.37	0.85*	1											
pH	0.73	-0.44	-0.02	0.17	0.81*	0.68	1										
Nitrate	-0.71	0.03	0.31	-0.25	-0.68	-0.92*	-0.48	1									
Nitrite	-0.11	0.76	-0.07	0.36	-0.11	0.27	-0.19	-0.49	1								
Alkalinity	0.52	0.07	-0.04	0.44	0.71	0.84*	0.47	-0.93*	0.52	1							
Phosphate	-0.54	0.09	0.75	-0.02	-0.29	-0.69	-0.05	0.77	-0.45	-0.55	1						
Iron (Fe)	-0.09	-0.39	-0.26	0.87*	0.58	0.44	0.37	-0.16	0.07	0.24	-0.03	1					
Copper (Cu)	-0.31	-0.52	-0.27	0.67	0.31	0.08	0.14	0.23	-0.30	-0.18	0.18	0.89*	1				
Zinc (Zn)	-0.47	0.11	0.56	-0.53	-0.64	-0.91*	-0.36	0.88*	-0.54	-0.80	0.82*	-0.51	-0.15	1			
Manganese	-0.55	-0.10	0.27	-0.41	-0.63	-0.89*	-0.42	0.97*	-0.64	-0.94*	0.74	-0.25	0.17	0.92*	1		
Lead (Pb)	0.03	-0.02	0.51	0.58	0.67	0.42	0.41	-0.41	0.14	0.69	0.14	0.48	0.21	-0.33	-0.46	1	
Cadmium	-0.81	0.053	0.63	0.05	-0.57	-0.7	-0.76	0.49	0.13	-0.25	0.46	-0.28	-0.14	0.51	0.40	0.15	1

Note: * means highly correlated parameters at P<0.05, DO in mg/l, salinity in ‰, Temperature in ^{0}C, heavy metals in mg/l, Conductivity in µS/cm,

Discussion

Spatial and temporal variations of physicochemical parameters and heavy metals were assessed from a textile-polluted River (Iya Alaro), Ikeja, Lagos. Summary of the mean variation of Physicochemical parameters are shown in Table 1, Water temperature is one of the most important characteristics of an aquatic ecosystem which affects dissolved oxygen levels, chemical processes, biological processes, and species composition; also affected is water density and stratification (Fink, 2005). In this study, the temperature of the river in dry season varied from 26.6 to 27.1°C and 25.5 to 26.1°C in wet season. Values recorded were above the WHO permissible limit (25°C), this may be a result of human activities and direct discharge of industrial waste into the river. Analysis of variance (ANOVA) shows that temperature values were significantly different ($P<0.05$). Pearson's Correlation matrix was used to assess the interactions among the parameters in which temperature was positively correlated with dissolved oxygen ($r=0.64$) and salinity ($r=0.46$); but was negative with carbondioxide ($r= -0.57$) and total hardness ($r= –0.12$). This result was relative to the report of Ahipathy (2006).

Wetzel, (2001) opined that Dissolved oxygen (DO) is a relative measure of the concentration of oxygen that is dissolved in the water or the amount of gaseous oxygen available to living aquatic organisms in the aquatic environment. Murphy, (2006) reported that DO is essential for the survival of fish and other aquatic organisms. The mean concentration of DO in this study ranged from 1.3mg/l (station 1) to 2.25mg/l (station 3) in the dry season. Wet season, 0.62mg/l (station 1) to 0.83mg/l (station 3). The results were far below the WHO permissible limit (5.0mg/l). The mean monthly variation for the three sampling stations varied significantly (ANOVA, $P<0.05$). Textile materials washed into the river during the rainy season increase and consequently affected the dissolved oxygen concentration. Biological effects and environmental changes associated with oxygen depletion may include: killing of aquatic life occurring abruptly in early morning, and species with high oxygen requirements (Meyer and Barclay, 1990). Also, carbondioxide had the highest values recorded in station 1 (Upper stream) which is closest to the textile industry (295.6±189.31mg/l) and (196.53±280.4mg/l) for both dry and wet season respectively. This levels in the sampling stations were above the WHO permissible limit (<10mg/l); and may be due to pollution from textile waste, domestic and other un-identified sources discharged into the river. Pollution produces high carbondioxide which gives fish hard time from getting the oxygen needed which can cause suffocation and death.

Although, Hutchinson, (1975) opined that most aquatic higher plants can utilize bicarbonate for photosynthesis. Alkalinity ranged from 177.2 (station 3) to 366.3mg/l (station 1) during the dry season, and 201.6 (station 3) to 279.8mg/l (station 1) in the wet season, these values exceeded the WHO limit (120mg/l). If a body of water has a high alkalinity, it can limit pH changes due to acid rain, pollution or other factors (EPA, 2012). Alkalinity in this study had strong and negative correlation with nitrate ($r=–0.93$); and positive with conductivity ($r=0.84$). The temporal variation showed low salinity in raining season when rainwater brought lots of fresh water from channels, rivers and streams, and high salinity in dry season. The results reported that the seasonal variations station 1, [upper stream], station 2 [mid-stream] and station 3 [lower stream] are highly varied at $P<0.05$. The total hardness shows the impact of run-off from rainfall, from point sources of pollution towards the down-stream (SS3). Total hardness weakly correlated with carbon dioxide ($r=0.39$) and negatively correlated with dissolved oxygen ($r=-0.35$). Salinity is the measure of dissolved salts in the river. The results implies that the river is a freshwater body. However, high concentration of salts can threaten aquatic ecosystems and their constituent species and also render the water unusable for human users (EPA, 2014). Salinity measured across the sampling stations did not vary significantly ($p<0.05$). It was stated by Estevez, et al., (2019) that the urbanization and agriculture are the main drivers of rivers and streams salinization.

Nitrate represents the most oxidize form of nitrogen and the product of oxidation of nitrogenous matters and its concentration may depend on the nitrification and de-nitrification activities micro-organisms. Nitrate for both dry and wet season as shown in table 2 and 3. The results shows high values from the point source of textile effluent which implies that the organic decomposition of textile effluent was minimal. The correlation coefficient value shows that nitrate concentration is negativity correlation with conductivity ($r=-0.92$). It was also observed in another study, the values of nitrate in both Little Akaki River and Great Akaki river to be 189.0±319.0 and 8.0±11.0mg/l respectively. High nitrate may be due to the natural abundance of nitrate ion in the sediment as part of nitrogen cycle (Beyene et. al., 2009). The mean nitrite concentration recorded throughout the sampling period varied significantly ($p<0.05$). The values did not exceed the standard limit for EDWQ and WHO (<1.0mg/l). However, the sources of nitrite in this river may be from naturally occurring rock decomposition and nitrogen containing organic matter. According to Getachew (2013), when compared to Sebata river, Ethiopia, it showed same trend of nitrite concentration (0.51mg/l). Nitrite correlated weakly with conductivity ($r=0.27$) and salinity ($r=0.36$).

Phosphate showed slight statistical variation (ANOVA) ($p<0.05$) throughout the sampling period. Phosphate (PO_4^{3-}) determination is useful in measuring water quality since it is an important plant nutrient and may play role of limiting factor among all other essential plant nutrients. Maximum values recorded was in SS2 (1.65±0.14mg/l) and station 1 (2.13±0.36mg/l) for dry and wet seasons respectively. Possibly, as a result of waste dislodging and phosphate-based fertilizers from agricultural activities. As opined by Walker et al., (2008), agricultural run-off increases concentration of phosphate along the streams. From the results, no spatial or temporal differences were observed (ANOVA). Phosphate however correlated with total hardness ($r=0.75$) and nitrate ($r=0.77$). According to Wondinmu and Tesso, (2011), reported that Huluka river Ambo Ethiopia, had 1.75mg/l of phosphate downstream and concluded that the source was from domestic and municipal waste discharged into the river. Similar assertions were made by Walker et al., (2006) and Mayer et al., (2008).

The maximum values recorded for conductivity (E.C) are observed in SS1 (upper stream) (1204.57±161.1µS/cm) and (755.33±345.79 µS/cm) for dry and wet season was above the WHO limit (500µS/cm). However, minimum values were recorded down-stream (SS3) (614.3±359.48µS/cm) in the dry season, while 477.7±430.96µS/cm was recorded in wet season. The values of electrical conductivity decrease as it flows downstream. The high values may be as a result of direct discharge of textile effluent, municipal and domestic waste. Mekonnen et. al., (2018) recorded a minimum of 171.2µS/cm (site A) and a maximum value of 1592.6µS/cm (site B). Results may be associated with textile effluent discharged from dissolved substances from soap and detergent factories, municipal effluent discharged from residential communities and chemicals applied to farmland. Statistical differences were observed among sample stations and study period. Electrical conductivity was strongly correlated with temperature ($r=0.85$). Wondinmu and Tesso, (2011) reported similar trend.

The significance of the study of pH in the aquatic ecosystem cannot be overemphasized. Since most of the chemical reactions in aquatic environment are controlled by any change in the value of pH. The pH of the river showed weakly acidic to neutral which lies within WHO limit (6.5–8.5). The maximum value was recorded in SS1 (7.14±0.56) for dry season and SS2 (7.1±0.36) for wet season. The results implies that pH value is life supportive for the aquatic organisms inhabiting the environment. There were significant differences in the concentration ($p<0.05$) during the sampling periods. PH strongly correlated with temperature ($r=0.81$) and dissolved oxygen ($r=0.73$). pH can also affect the solubility and toxicity of chemicals and heavy metals in the water (EPA, 2012).

Heavy metals results as reported in table 2, showed concentrations in surface water and sediments are opined to be influenced by impute from source, the character of sediment, organic materials, temperature and sometimes the mineral composition of underlying rocks in the area where surface water is situated. Thus, spatial and temporal variation in heavy metals concentration in sediments and especially in water should be naturally expected (Amadi et al., (2014) and Tonko, (1989). In the present study, significant variations are indicated by the concentration of the metals with high standard deviation shown at different sites. Mean iron [Fe] concentration of the studied river ranged from 1.43mg/l (wet season) to 2.97mg/l (dry season). When compared with the maximum permissible limit of WHO, iron concentration in the entire river was above the maximum acceptability unit (0.3mg/l). A decrease in concentration of iron was observed from upstream to downstream. This may be due to iron tendency to form complex compounds with anions and could settle in the river bed. Pearson correlating coefficient shows that iron was strongly correlated ($r>0.5$) with zinc ($r=0.82$). The result showed that the most polluted area of the river is SS1 being the hotspot/ point source of textile effluent dislodge amongst other pollutants. While lower values were obtained from the middle stream and downstream respectively due to dilution, runoffs, sedimentations, etc.

The mean concentration of copper (Cu) in the water samples under the study ranged from 0.01mg/l (wet season) to 0.03mg/l (dry season). None of the values of the sample stations in the river analyzed were above the recommended limit (0.5mg/l) of WHO guidelines. However, during the sampling period, the concentration of copper is not significantly different ($p>0.05$). Copper strongly correlated with iron ($r=0.89$). According to Deepali et al., (2010), a lower concentration of copper (0.01mg/l) was recorded in effluents of textile factory located near Haridwar, India and when compared to the studied river follows the same trend. The low levels of copper recorded may be attributed to the natural purification processes within the river.

Zinc is an important trace element required by many aquatic organisms in low quantity and it plays a vital role in the physiological and metabolic process of many organisms. Although in the studied river, values were measured above the WHO standard limit (0.2mg/l). The maximum values observed in station 1 for both dry season and wet season (0.96±0.47mg/l and 2.36±0.66mg/l) may be due to the discharge from nearby textile industries. Statistical differences (ANOVA) were observed throughout the sampling duration. Zinc strongly correlated with nitrate ($r=0.88$), phosphate ($r=0.82$) and strongly negatively correlated with conductivity ($r=-0.91$). A high concentration of zinc is known to be harmful because it causes phytotoxicity and affects the body's functions such as reproduction, skin health, sense of taste and smell, brain functions and growth. Yusuff and Sonibare (2004) reported similar concentrations of Zinc which ranged from a minimum of 0.19mg/l to 0.36mg/l from textile effluent in Kaduna, Nigeria and Ohioma et al., (2009) recorded the highest concentration of Zinc from textile factories from the same state as compared to the present study. The mean values for manganese in water samples for both dry season and wet season ranged from 0.06±0.05mg/l (SS1) to 0.29±0.12mg/l (SS3) and from 0.19±0.17mg/l (SS1) to 0.29±0.12mg/l (SS3) respectively. The values recorded for manganese were below the standard limit set by WHO (0.5mg/l). The maximum value recorded was probably from the natural decomposition of manganese-containing. A decrease in manganese concentration was observed as it flows downstream. Concentration of manganese varied significantly ($p<0.05$) throughout the sampling period. Manganese strongly correlated with zinc ($r=0.92$), nitrate ($r=0.97$) and negatively with conductivity ($r=-0.89$) and alkalinity ($r=-0.94$). High manganese uptake can cause tremors and coordination failures (Vieira et al., 2012).

Lead accumulation can cause oxidative stress and may lead to death. The results for the three sampling stations were above the standard limit for EDWQ and WHO (0.01mg/l). Highest values were recorded in station 1 (0.04±0.02mg/l) in dry season and (0.03±0.02mg/l) in the wet season. Lead correlated with alkalinity ($r=0.69$). The concentration of lead is not significantly different ($p>0.05$) throughout the study period. Also, cadmium concentration in the three sampling stations were above the standard limit set by WHO (0.01mg/l). The highest value recorded in station 1 (0.01±0.001mg/l) and (0.03±0.02) for both dry and wet season may be due to the frequent disposal of waste and leaching of contaminated sites around the location. Manganese varied significantly ($p<0.05$) among the three sampling stations. The mean concentration of cadmium correlated strongly with dissolved oxygen ($r=-0.81$).

Conclusion and Recommendation

From the results and comparism from above, the following conclusions are drawn: Physicochemical parameters and heavy metals from the studied river (Iya Alaro River) varied significantly throughout the sampling period. The variations observed was as a result of different sources of textile waste discharged into the upstream (SS1) where values recorded were significantly higher than SS2 (mid-stream) and SS3(down-stream). It was observed that the physicochemical parameters and heavy metals were above the permissible limit of WHO. Pollution level of the three sampling stations of the river follows the order, station 1>2>3. Though, the sample water tested were found to be rich in plant nutrients required for plant growth, but due to the presence of high level toxic heavy metals such as iron, copper, manganese, lead and cadmium, the river water is concluded not suitable for fish survival, irrigation, or for domestic purposes. This study indicates that there is a need to protect the quality of the river system. Therefore, it recommended that the government and other responsible authorities have to take appropriate corrective actions and should support further study for quick intervention and close monitoring to solve the growing environmental pollution and associated problems in Iya Alaro River.

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