



Determination of Selected Water Quality Parameters in River Sio, Busia County, Kenya

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Authors' contributions

This work was carried out in collaboration among all authors. Author KOO designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors JKK and AOO supervised the research while authors SMS, BEO and JKO managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Water samples were taken from five sampling points and their quality assessed through analysis of physical and chemical characteristics. Turbidity, temperature, conductivity, pH, dissolved oxygen and total suspended solids were determined on site during sample collection, using portable meters. Anions were determined using UV/Visible spectroscopy while heavy metals were determined using flame Atomic Absorption Spectroscopy (AAS) in accordance with AWWA standard methods. Turbidity was the highest recorded parameter during the wet season with a mean of 481.83 NTU. 53% of the parameters showed significant seasonal variation ($P < 0.5$) with the mean concentration of 56 % of the parameters being higher during the wet season. The parameters that exceeded the WHO limit were turbidity, phosphates, lead, iron, nickel, chromium and cobalt indicating poor quality of water in River Sio. Poor agricultural practices, domestic and industrial wastewater are the main factors that contribute to pollution of the River. The study proposes proper land use, proper treatment and disposal of sewage and use of organic manure and biological control as means of preventing water and soil pollution.

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1. INTRODUCTION

Due to increased population, industrialization, use of fertilizers and human activities, water is highly polluted with different harmful contaminants. It is necessary that the quality of drinking water be checked at regular time intervals, because due to the use of contaminated drinking water, human population suffers from water borne diseases like cholera, bilharzia and dysentery [1]. Natural water contains different types of impurities which are introduced into the aquatic system through weathering of rocks and leaching of soils, dissolution of aerosol particles from the atmosphere and from several human activities including mining, processing and the use of metal based materials [2]. Kenya is among the countries classified as facing serious scarcity of water with low fresh water endowment of 526m³ per capita per year [3]. Globally, a country is considered water scarce if its renewable fresh water supplies are less than 1000m³ per capita per year [4]. Despite such small amount of water available in the country, there has been a continuous release of toxic substances like heavy metals, insecticides, pesticides, raw sewage and fertilizers into the fresh water systems making water unfit for industrial, agricultural and domestic consumption. In the developing countries, water pollution and declining water quality is fast becoming a problem that if goes unchecked will have a negative impact on the ecosystem and natural water systems like the river sources [5]. There are extensive anthropogenic activities along River Sio which lead to pollution of the river. There are maize and sugarcane farms located upstream of River Sio. The increase in population of Busia County with poor sewer systems has led to an increase in wastes that are dumped in the river hence leading to an increase in the level of pollutants in the river. In terms of land use along river Sio, small scale farming accounts for 24.2%, wetland patches account for 40%, bush land patches account for 32% and grassland patches account for 15.1% [6].

2. MATERIALS AND METHODS

2.1 Study Area

River Sio originates from Kaujai and Luucho Hills in Bungoma County at an altitude of 1800m and

flows through Busia County into Berkeley Bay and drains into Lake Victoria in Uganda at an altitude of 1134m. The river flows through valleys as it cuts through forests, maize and sugarcane plantations into the lower densely populated and agricultural section of the catchment. The upper zone consists of maize and sugarcane plantations and land use in this zone is mainly agricultural. The second zone consists of sand harvesting area below the Musomabridge, where Western Sugar Company draws water from the river for cooling and washing machines. The third zone consists of maize and sugarcane plantations next to the Busia sugar company. Sand harvesting is also heavily practiced in this region. The fourth region is in Busia town, where the river flows through Mundika and water from the river is abstracted and directed towards Western Water and Sewerage Company treatment plant to supply tap water to the residents of Busia County. This region is densely populated with no sewerage system. The fifth zone consists of maize, millet and sorghum plantations. Fig. 1 shows a map of River Sio, with the counties through which the river traverses marked in light green while River Sio is marked in blue.

2.2 Sampling Method

Sampling was done during the dry season in January 2018 and during the wet season in May 2018. Dry season refers to the period between January and March, when temperatures are as high as 95°F. This period is characterized by lack of rainfall. Wet season refers to the period between April and June when the study area receives a lot of rainfall, usually above 1200 mm. Identification of sampling points to gather information on the possible sources of pollutants was done prior to sampling. The choice of sampling points was based on the areas where significant land change use had occurred [7]. 1000 mL grab samples of water were collected using simple random sampling methods during both the dry and the wet seasons. The grab water samples were collected in polyethylene bottles prewashed with detergents, 10% nitric acid and de-ionized distilled water [8].

2.3 Determination of Physico-chemical Parameters

Physico-chemical parameters like pH, temperature, turbidity, dissolved oxygen and

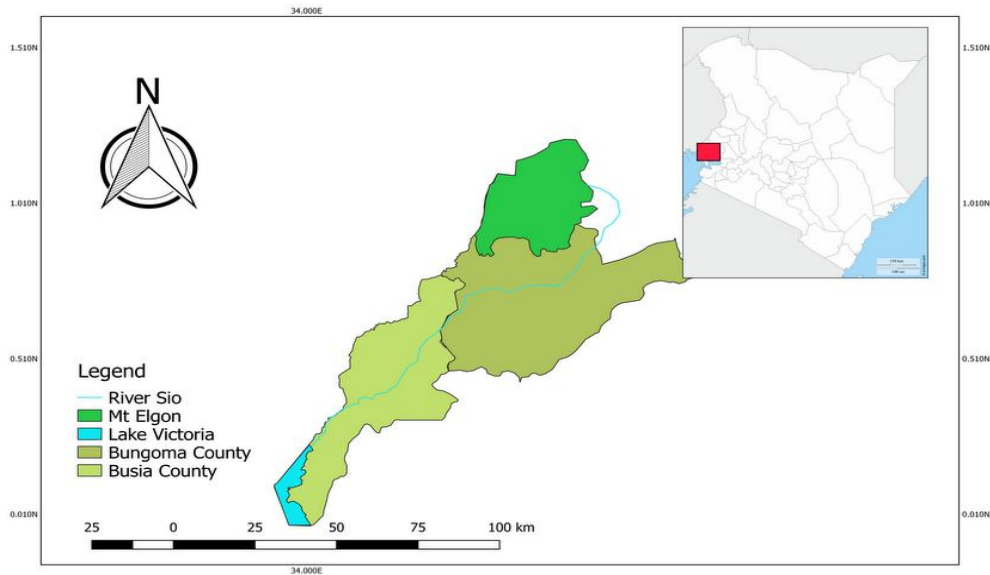


Fig. 1. Map showing River Sio

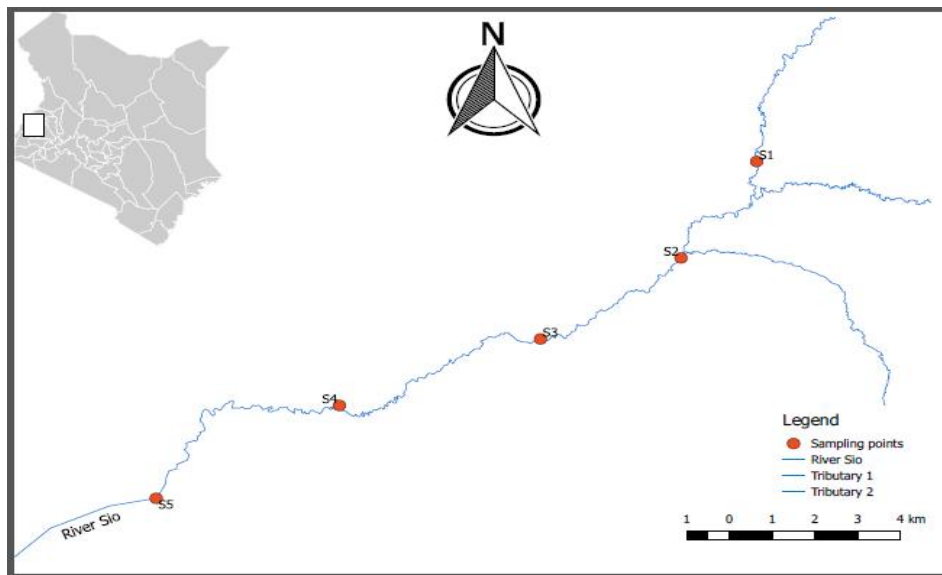


Fig. 2. Sampling points along River Sio

Table 1. Sampling stations descriptions and codes

Station	Description
S1	River Sio at Malomba bridge, next to sugarcane and maize plantations
S2	River Sio at Musoma bridge, where Western sugar company abstracts water for cooling engines
S3	River Sio at Busibwabo, next to Busia sugar company
S4	River Sio at Mundika bridge, where the River crosses Busia town next to Busia water company treating plant
S5	River Sio few kilometers from Busia town, downstream next to maize plantations

*S = Station

electrical conductivity were measured using portable meters according to standard methods for the analysis of waste water by the American Public Health Association [8].

2.4 Determination of Anions

500 mL grab samples of water were collected using simple random sampling methods during both the dry and the wet seasons. After transportation to the laboratory, the samples were stored at 4°C for 24 hours to minimize physicochemical changes [9]. The anions analyzed were nitrates, phosphates, sulphates and chlorides. They were determined using Shimadzu 1800 ultraviolet/visible spectrophotometer.

2.5 Determination of Heavy Metals

1000mL grab samples of water were collected using simple random sampling methods during both seasons. After transportation to the laboratory, the samples were stored at 4°C for 24 hours to minimize physicochemical changes [9]. Water sample for metal analysis was collected in clean plastic bottles and acidified with 1-2 drops of 65% nitric acid per litre to a pH of about 2.0 to minimize precipitation and adsorption on container walls [8]. Nitric acid digestion procedure was used whereby 100 mL of the water sample was treated with 5 mL Nitric acid and slowly heated on a hot plate to reduce the volume to 20 mL. The remaining solution was filtered and topped to mark in a 100 mL volumetric flask [8] and the levels of heavy metals determined using Shimadzu 6200 flame Atomic Absorption Spectrophotometer.

3. RESULTS AND DISCUSSION

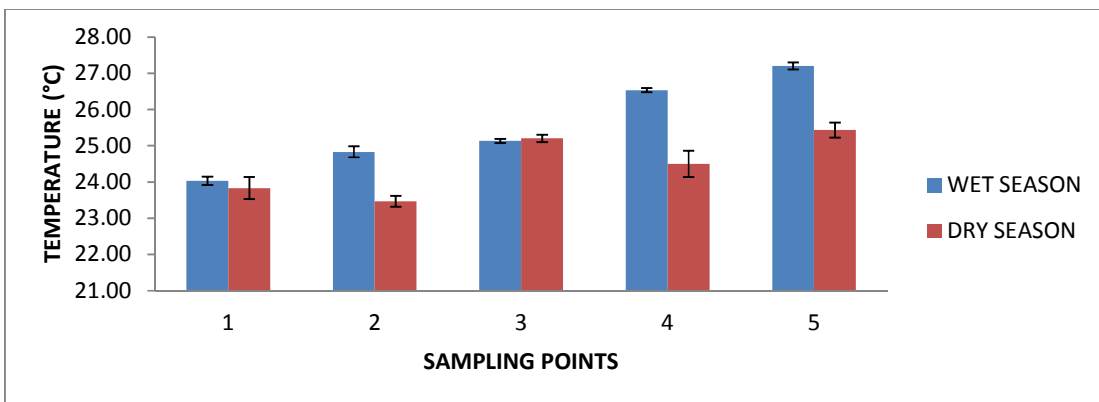
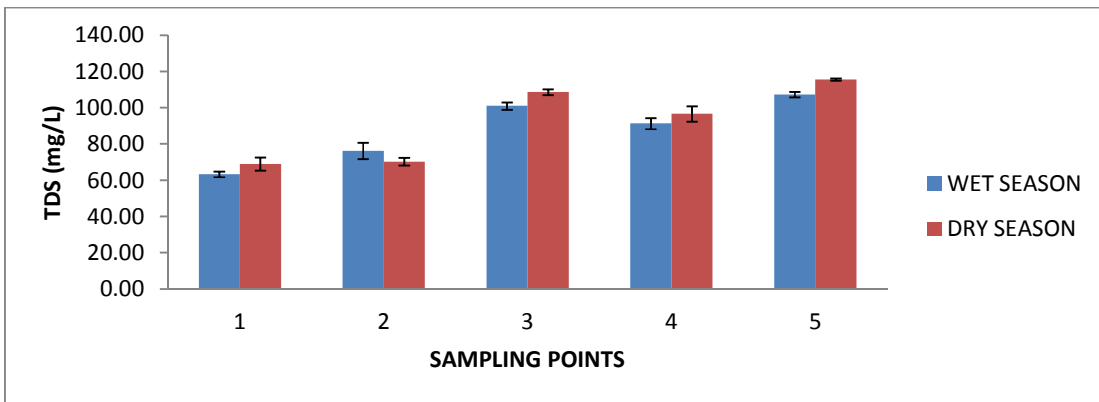
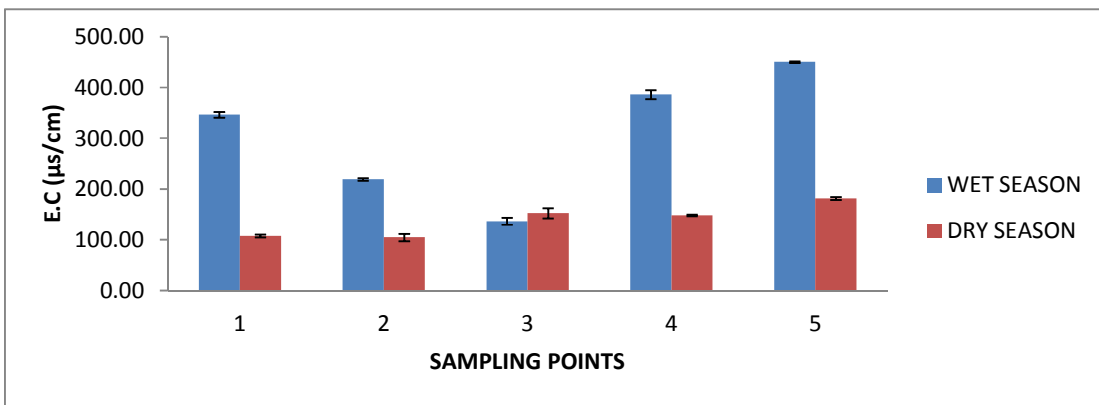
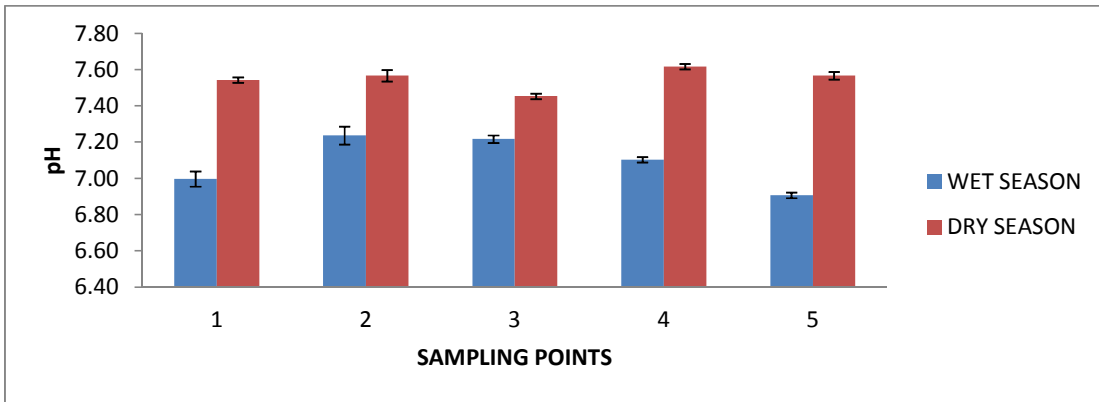
3.1 Physico-chemical Parameters

Temperature range for water was 23.47±0.15°C to 25.43±0.21°C during the dry season and 24.03±0.12°C to 27.20±0.10°C during the wet season. The high temperatures during the wet season can be attributed to an increase in suspended particles which absorb sunlight, leading to an increase in water temperature during the wet season. According to paired t-test, the dry and wet seasons were not significantly different while as per one way ANOVA, the spatial variations of temperature were statistically significant as shown in Tables 3 and 4 respectively. The $T_{\text{calculated}}$ value was 2.51 while

the T_{critical} value was 2.78 at $P = .05$ as per the paired t-test. Since the $T_{\text{calculated}} < T_{\text{critical}}$ there was no significant difference in temperature between the dry and the wet season. According to one way ANOVA, $F_{\text{calculated}}$ was 35.91 during the dry season and 469.45 during the wet season, while F_{critical} was 4.76 at $P = .05$. Since $F_{\text{calculated}} > F_{\text{critical}}$ the spatial variations in temperature were statistically significant and this was attributed to the altitude at which sampling was done, weather conditions and the time of the day when sampling was done. Similar results for temperature were also obtained during the determination of physicochemical and microbiological parameters of water from Rivers in Keffi, central Nigeria [10].

The pH range was between 7.45±0.02 to 7.62±0.02 during the dry season and 6.70±0.04 to 7.24±0.05 during the wet season. All the five sampling points were within the 6.5 – 8.5 pH range allowed by the WHO. There was a significant difference in seasonal variation with a $T_{\text{calculated}}$ value of 5.89 against a T_{critical} value of 2.78 at $P = .05$ for paired t-test. Since $T_{\text{calculated}} > T_{\text{critical}}$ there was a significant difference in pH between the dry and wet seasons. Spatial variations were significantly different during the dry and wet seasons showing slight alkalinity in all the five sampling stations during the dry season. Pollution from domestic and industrial waste water is the cause for the slight alkalinity in the River water during the dry season [11]. Similar pH ranges for both the wet and dry seasons were reported during the assessment of physicochemical property of Okoro River estuary, south eastern Nigeria [12].

Electrical conductivity ranged from 105.00±7.21 to 181.67±2.89 $\mu\text{S}/\text{cm}$ during the dry season and 136.67±6.66 to 450.33±1.53 $\mu\text{S}/\text{cm}$ during the wet season. Paired t-test revealed significant difference in electrical conductivity during both the wet and dry seasons. $T_{\text{calculated}} = 3.17 > T_{\text{critical}} = 2.78$ ($P = .05$). Spatial variations were statistically significant during both the wet and dry seasons as per one way ANOVA. During the dry season, $F_{\text{calculated}} = 91.62$ and during the wet season, $F_{\text{calculated}} = 1473.75$, while $F_{\text{critical}} = 3.48$ ($P = .05$). Since $F_{\text{calculated}} > F_{\text{critical}}$ for both the dry and wet seasons, the spatial variations in electrical conductivity were statistically significant at $P = .05$. The rise in electrical conductivity during the wet season can be attributed to surface run-off which carries dissolved minerals from the farms into the river during the wet season. The high values of electrical conductivity



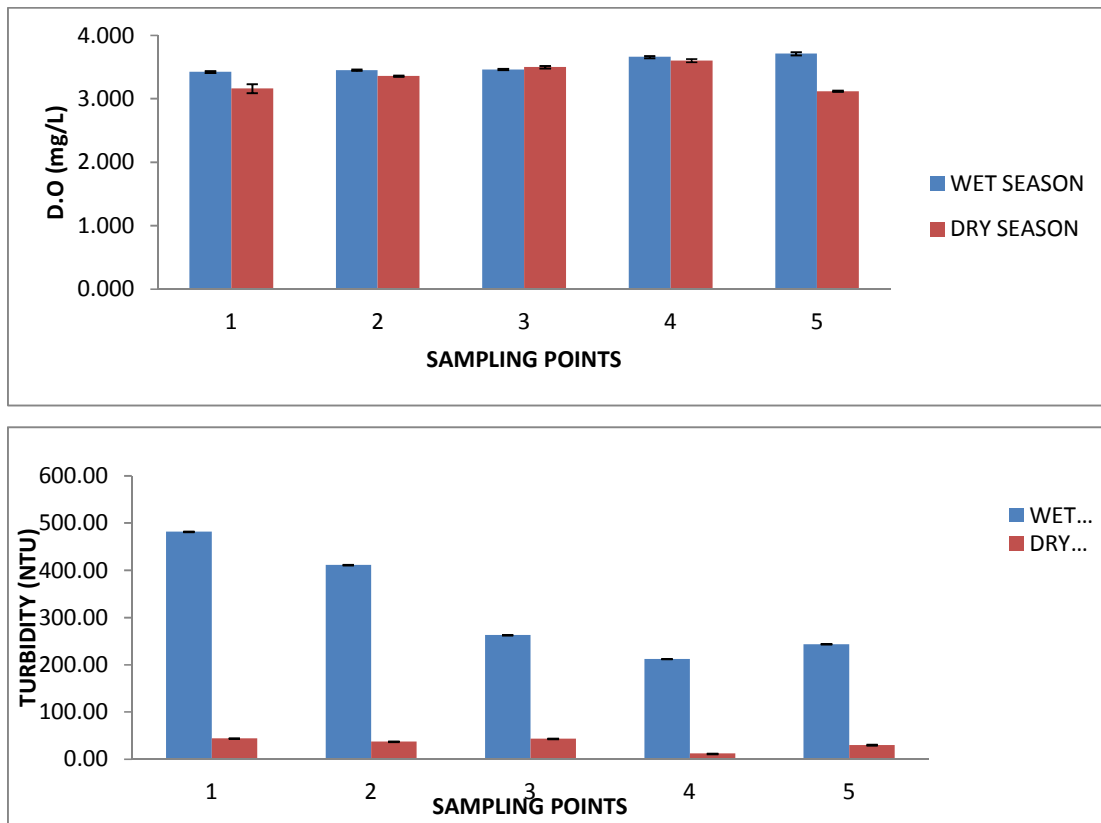


Fig. 3. Bar graphs showing trends in seasonal variation in physico-chemical parameters

downstream can be attributed to increased anthropogenic activities such as sand mining, cultivation and laundry along the river. Electrical conductivity was within the WHO guideline limits. The similar range of electrical conductivity during the dry season was reported in the assessment of water quality for Goro Dong and its sustainability for consumption and domestic use by the immediate Lake communities in Numan, Adamawa state Nigeria [13].

TDS values during both the dry and wet seasons were found to be below the WHO recommended standards for drinking water. TDS values varied from 69.00 ± 3.61 mg/l to 115.67 ± 0.58 mg/l during the dry season and 63.33 ± 1.5 mg/l to 107.33 ± 1.5 mg/l during the wet season. Paired t-test established no significant difference in TDS between the dry and wet seasons. $T_{\text{calculated}} = 1.61 < T_{\text{critical}} = 2.78$ at $P = .05$. One way ANOVA established a significant difference in spatial variations during both the dry and wet seasons. $F_{\text{calculated}} = 186.64$ and 127.01 during the dry and wet seasons respectively, while $F_{\text{critical}} = 3.49$ at

$P = .05$. Since $F_{\text{calculated}} > F_{\text{critical}}$ for both seasons, the spatial variations in TDS were statistically significant at $P = .05$. The slight increase in TDS during the dry season can be attributed to evaporation of water during the dry season, leading to a low water volume in the river hence a rise in TDS. The high values of TDS downstream can be attributed to increased anthropogenic activities such as sand mining, cultivation, bathing and laundry along the river.

Turbidity values ranged from 12.03 ± 0.61 NTU to 44.33 ± 0.5 NTU during the dry season and 212.50 ± 0.50 NTU to 481.83 ± 0.76 NTU during the wet season. The recommended mean turbidity value is 0.1 NTU and any value above this will mask microorganisms from disinfection during water treatment and stimulate microbial growth as well. This is due to the fact that nutrients are adsorbed onto particulate surfaces thereby enabling the attached bacteria to grow more rapidly than those in free suspension. The WHO accepted level of turbidity in drinking water is 5 NTU [14]. Turbidity was above the WHO

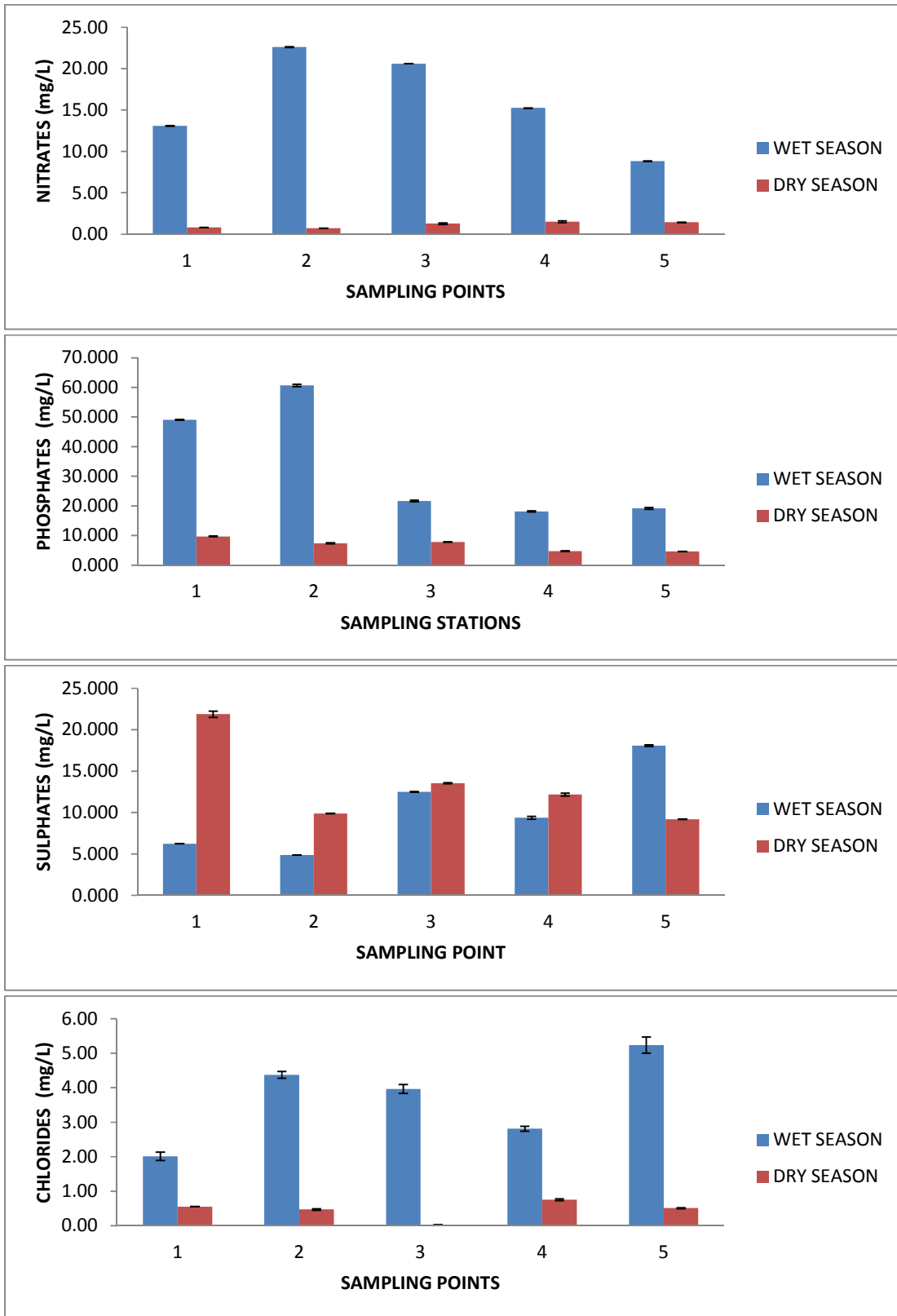


Fig. 4. Bar graphs showing trends in seasonal variation in anions

recommended limit of 5 NTU during both the dry and wet seasons, with sampling station 1 recording the highest turbidity values during both seasons. Paired t-test revealed a significant difference in turbidity during both the dry and wet seasons, with $T_{\text{calculated}} = 5.92 > T_{\text{critical}} = 2.78$ at $P = .05$. One way ANOVA revealed spatial variations of turbidity to be significant since $F_{\text{calculated}} > F_{\text{critical}}$, with $F_{\text{calculated}} = 1,242.47$ and $107,883.10$ for dry and wet season respectively, while $F_{\text{critical}} = 3.48$ at $P = .05$. The high levels of turbidity during the wet season can be attributed to surface run-off from sediments due to poor agricultural practices upstream.

Dissolved oxygen refers to the volume of oxygen present in water and it is an indicator of the health of the ecosystem. Exposure of organisms to oxygen levels of less than 2 mg/l for 1-4 days may kill most of the aquatic life in the system [15]. DO ranged from 3.12 ± 0.01 mg/l to 3.60 ± 0.03 mg/l during the dry season and 3.42 ± 0.02 mg/l to 3.71 ± 0.03 mg/l during the wet season. Paired t-test revealed no significant difference in the levels of DO between the dry and wet seasons, since $T_{\text{calculated}} < T_{\text{critical}}$ with $T_{\text{calculated}} = 1.72 < T_{\text{critical}} = 2.78$ at $P = .05$. One way ANOVA showed spatial variations to be statistically significant, since $F_{\text{calculated}} > F_{\text{critical}}$ for both seasons at $P = .05$. $F_{\text{calculated}} = 106.13$ and 186.83 for dry and wet seasons respectively, while $F_{\text{critical}} = 3.48$ at $P = 0.05$.

3.2 Anions

Nitrates ranged from 0.74 ± 0.02 mg/l to 1.52 ± 0.12 mg/l during the dry season and 8.84 ± 0.011 mg/l to 22.61 ± 0.058 mg/l during the wet season. Seasonal variations of nitrates were found to be statistically significant with $T_{\text{calculated}} > T_{\text{critical}}$. $T_{\text{calculated}} = 5.79 > T_{\text{critical}} = 2.78$ at $P = .05$. Spatial variations were also found to be statistically significant with $F_{\text{calculated}} > F_{\text{critical}}$ where $F_{\text{calculated}} = 80.01$ and $108,793.20$ during the dry and wet seasons respectively, while $F_{\text{critical}} = 3.48$ at $P = .05$. Nitrate levels were below the WHO limit of 50 mg/l during both dry and wet seasons. The high concentration of nitrates during the wet season can be attributed to surface run-off carrying manure, fertilizers and domestic waste from the sugarcane and maize plantations located at the banks of the river. The high nitrate concentration downstream during the dry season can be explained by disposal of domestic sewage as the river flows through the densely populated region of Busia town. Nitrates stimulate the growth of macrophytes and

phytoplankton and if left unchecked can lead to eutrophication of water bodies [15].

Sulphates get into soil via soil minerals atmospheric depositions, fertilizers and pesticides. They may also be found in surface water as an industrial pollutant commonly from coal mining, industrial wastes and sewage and streams draining from coal or metal-sulfide mines. In large amounts, sulfates can result in bitter, medicinal tastes, laxative effects or "rotten egg" odor from hydrogen sulfide gas formation [16]. The concentration of sulphates ranged from 9.19 ± 0.04 mg/l to 21.87 ± 0.38 mg/l during the dry season and 4.87 ± 0.00 mg/l to 18.08 ± 0.10 mg/l during the wet season. The high concentration of sulphates at sampling station 5 during the wet season can be linked to surface run-off containing ammonium sulphate fertilizers and domestic waste water discharges. Seasonal variations were not statistically significant with $T_{\text{calculated}} = 0.79 < T_{\text{critical}} = 2.78$ at $P = .05$. Spatial variations were found to be statistically significant at $P = .05$, with $F_{\text{calculated}} = 2252.00$ and 9782.69 for dry and wet season respectively, while $F_{\text{critical}} = 3.48$. Sulphate concentration in all the five sampling stations was found to be below the WHO guideline limit of 250 mg/l.

Phosphorus finds its way into surface waters from fertilizer run-off due to agricultural activities, erosion of rocks/mining, and domestic waste due to the use of detergents, industrial waste and also due to decaying of organic matter of plant and animal origin. Phosphorus is an algal nutrient which contributes to excess algal growth and eutrophication [17]. Phosphorus concentration ranged from 4.61 ± 0.05 mg/l to 9.71 ± 0.04 mg/l during the dry season and 18.13 ± 0.21 mg/l to 60.65 ± 0.39 mg/l during the wet season. Seasonal variation was statistically significant, with $T_{\text{calculated}} = 3.27 > T_{\text{critical}} = 2.78$ at $P = .05$. Spatial variations were found to be statistically significant with $F_{\text{calculated}} = 1395.64$ and $15,480.90$ for dry and wet season respectively, while $F_{\text{critical}} = 3.48$ at $P = .05$. The high concentration during the wet season can be attributed to leaching of phosphorus in the form of surface run-off into the river as a result of agriculture as well as domestic waste and raw sewage that is discharged into the river due to lack of proper sewerage system. The increasing trend upstream can be attributed to change in land use, as agricultural areas contribute more phosphates due to the use of phosphorus based fertilizers like ammonium phosphate. The concentration of phosphates was above the

WHO recommended limit of 5 mg/l in all the sampling stations during both the wet and dry seasons, apart from sampling stations 4 and 5 whose concentrations were below the WHO recommended limit during the dry season, and this can be attributed to reduced laundry activities at these stations leading to less surfactants getting into the river.

Chloride concentration ranged from 0.03 ± 0.01 mg/l to 0.76 ± 0.02 mg/l during the dry season and 2.01 ± 0.12 mg/l to 5.23 ± 0.24 mg/l during the wet season. Both seasonal and spatial variations were found to be statistically significant at $P = .05$. However, chloride concentrations were found to be far below the WHO recommended limit of 250 mg/l. Paired t-test revealed $T_{\text{calculated}} = 5.17 > T_{\text{critical}} = 2.78$ at $P = .05$. One way ANOVA revealed $F_{\text{calculated}} = 792.25$ and 241.08 for dry and wet season respectively $> F_{\text{critical}} = 3.48$ at $P = .05$. The high chloride concentration during the wet season can be attributed to surface run-off from anthropogenic sources like raw sewage, animal waste and chloride based inorganic fertilizers like potassium chloride [18].

3.3 Heavy Metals

Both natural processes and anthropogenic activities are the main sources of surface and ground water contamination by heavy metals. Increase in heavy metal concentration in water is becoming a serious threat to human health and aquatic ecosystems [19]. Lead is usually present in surface water from industrial pollution. High level of lead leads to cognitive impairment in children to peripheral neuropathy in adults [20]. Symptoms of lead poisoning range from gastrointestinal disturbances to inflammation of the brain and spinal cord [16]. Lead was only reported in four stations during the wet season, as the concentration of lead was below detection limit in all the other stations during both the dry and wet seasons. The presence of lead in stations S2, S3, S4 and S5 during the wet season can be attributed to run-off from garages, workshops in the shopping centers and market places within the catchment, and sewage effluent washed away by run-off. Similar findings for lead were reported during the determination of selected water quality parameters in the Chania River catchment, Kenya [14]. The levels of lead detected at these points were above the recommended WHO limit of 0.01 mg/l hence posing a health risk to aquatic life in the river as well as users of water from the river.

Cadmium occurs in combined form with other non-metallic elements such as sulphur, oxygen and chlorine. Cadmium hardens and toughens tissues leading to destruction of organs. Cadmium poisoning leads to low sperm count in men and reduced fertility in women. Cadmium is primarily found in surface water as a pollutant from industries such as the electroplating industry [16]. The levels of cadmium in all the stations were found to be below the limit of detection during both seasons, indicating no pollution from cadmium.

Iron concentration ranged from 2.93 ± 0.08 mg/l to 4.29 ± 0.09 mg/l during the dry season and 8.78 ± 0.13 mg/l to 13.73 ± 0.18 mg/l during the wet season. The t-test results indicated there was significant difference between the dry and wet seasons, with $T_{\text{calculated}} = 6.79 > T_{\text{critical}} = 2.78$ at $P = .05$. One way ANOVA indicated spatial difference to be statistically significant, with $F_{\text{calculated}} = 82.99$ and 125.86 during the dry and wet seasons respectively and this was greater than $F_{\text{critical}} = 3.49$ at $P = .05$. The high iron concentrations observed during the wet season can be attributed to weathering of rocks, run-off from construction sites and garages and from sediments which are deposited into the river during the wet season. The concentration of iron was above the WHO recommended limit of 0.3 mg/l during both the dry and wet seasons. High concentration of iron in water stains laundry and plumbing fixtures. Iron concentration of above 0.3 mg/l in water produces a noticeable iron taste in water [14]. High levels of iron during the wet season were also reported during the assessment of water quality in Surma River, Bangladesh [21].

Zinc occurs naturally in water, but it may also result from industrial pollution. Low water pH can also result in the release of zinc due to the corrosion of copper-zinc alloys used in plumbing systems. Zinc can produce a chalky appearance in water and produce a disagreeable taste [16]. Zinc levels in water ranged from 0.13 ± 0.01 mg/l to 0.27 ± 0.01 mg/l during the dry season, to 0.10 ± 0.01 mg/l to 0.33 ± 0.01 mg/l during the wet season. There was no significant difference in seasonal variation between the dry and wet seasons. According to paired t-test, $T_{\text{calculated}} = 0.49 < T_{\text{critical}} = 2.78$ at $P = .05$. The spatial variations were significantly different, with $F_{\text{calculated}} = 132.23$ and 137.62 during the dry and wet seasons respectively and this was greater than $F_{\text{critical}} = 3.49$ at $P = .05$. The level of zinc in

all the five stations was below the WHO recommended limit of 3.0 mg/l.

Copper is introduced into water systems via contamination from mining, acid waters and corrosions in copper plumbing. Copper poisoning includes such symptoms as jaundice and anemia. High levels of copper in water may cause staining and bad taste, in addition to corrosion [16]. The concentration of copper ranged from 0.52 ± 0.03 mg/l to 0.60 ± 0.02 mg/l during the dry season and 0.08 ± 0.01 mg/l to 0.34 ± 0.02 mg/l during the wet season. Seasonal variation was statistically significant, with $T_{\text{calculated}} = 6.88 > T_{\text{critical}} = 2.78$ at $P = .05$. Spatial variations were statistically significant, with $F_{\text{calculated}} = 7.10$ and 226.14 during the dry and wet seasons respectively and this was greater than $F_{\text{critical}} = 3.49$ at $P = .05$. The high concentrations during the dry season can be attributed to evaporation of water from the river, leading to a lower volume of the river water as compared to dilution during the wet season. The level of copper in all the five stations was below the WHO recommended limit of 1.0 – 2.0 mg/l. Similar concentrations of copper in water were reported during the evaluation of irrigation water quality from major water sources in Ondo and Osun states, Nigeria [22].

Manganese is found in dissolved form in shale, sandstone or river basin material. Excess manganese gives water a grayish/black appearance and as a result may stain plumbing fixtures and laundry [16]. Manganese levels ranged from 0.22 ± 0.01 mg/l to 0.50 ± 0.02 mg/l during the dry season and 0.19 ± 0.01 mg/l to 0.26 ± 0.01 mg/l during the wet season. There was no significant difference in seasonal variations as paired t-test revealed $T_{\text{calculated}} = 2.02 < T_{\text{critical}} = 2.78$ at $P = .05$. Spatial variations were statistically significant as per one way ANOVA, with $F_{\text{calculated}} = 62.31$ and 7.52 during the dry and wet seasons respectively and this was greater than $F_{\text{critical}} = 3.49$ at $P = .05$. All the stations recorded manganese concentration that was below the recommended WHO limit of 0.4 mg/l with the exception of station 4 during the dry season. The high concentration of manganese at station 4 can be linked to garbage disposal and domestic waste water that is discharged into the river at station 4. Concentrations of manganese in River water ranging from 0.02 – 0.68 mg/l were reported during pollution studies of heavy metals in Warri River, Delta state, Nigeria [23].

Nickel occurs naturally in ground and surface water as an industrial or mining pollutant.

Chronic exposure to nickel causes decreased body weight, heart and liver damage and dermatitis [16]. Nickel concentration ranged from 0.35 ± 0.03 mg/l to 0.94 ± 0.05 mg/l during the dry season and 0.13 ± 0.01 mg/l to 0.35 ± 0.01 mg/l during the wet season. Paired t-test pointed to the lack of significant difference in seasonal variation, with $T_{\text{calculated}} = 2.57 < T_{\text{critical}} = 2.78$ at $P = .05$. However, spatial variations were found to be statistically significant with one way ANOVA giving values of $F_{\text{calculated}} = 121.91$ and 31.11 during the dry and wet seasons respectively and this was greater than $F_{\text{critical}} = 3.49$ at $P = .05$. All the stations recorded nickel values that were above the recommended WHO limits of 0.07 mg/l during both the dry and wet seasons. These high concentrations can be linked to sand mining along the banks of the river, run-off from garages and untreated sewage since nickel can be excreted from human faeces and urine. Similar patterns in the concentration of nickel in River water during dry and wet seasons were reported during the assessment of physicochemical property of Okoro River estuary, south eastern Nigeria.

Chromium is naturally found in ground and surface water as an industrial pollutant mainly from the electroplating industry. Chromium causes skin irritations when one is externally exposed. When internal exposure occurs, kidney and liver damage may occur [16]. Chromium concentration ranged from 0.03 ± 0.01 mg/l to 0.10 ± 0.01 mg/l during the dry season and 0.04 ± 0.00 mg/l to 0.29 ± 0.01 mg/l during the wet season. Seasonal variations showed no significant difference between the dry and wet seasons with $T_{\text{calculated}} = 2.72 < T_{\text{critical}} = 2.78$ at $P = .05$. There was a significant difference in spatial variations, with $F_{\text{calculated}} = 48.77$ and 394.89 during the dry and wet seasons respectively and this was greater than $F_{\text{critical}} = 3.49$ at $P = .05$. Only station 1 recorded chromium concentrations below the WHO recommended limits of 0.05 mg/l during the dry and wet seasons, while station 2 recorded chromium concentrations that were below the WHO recommended levels only during the dry season. All the remaining stations recorded chromium concentrations above the WHO recommended levels of 0.05 mg/l. The concentration of chromium increased downstream during the wet season. The high values during the wet season can be linked to run-off that washed away chromium containing paints into the river and also via leaching of chromium from top soil and rocks. Similar results

Table 2. Metal ion concentration - wet and dry seasons

Parameter	Season	S1	S2	S3	S4	S5	WHO	KEBS
Lead mg/l	WET	< DL	0.38±0.00	0.40±0.02	0.55±0.03	0.33±0.02		
	DRY	< DL	< DL	< DL	< DL	< DL	0.01	0.05
Manganese mg/l	WET	0.22±0.01	0.25±0.04	0.26±0.01	0.19±0.01	0.26±0.01		
	DRY	0.22±0.01	0.29±0.01	0.36±0.04	0.50±0.02	0.35±0.02	0.4	0.1
Cadmium mg/l	WET	< DL	< DL	< DL	< DL	< DL		
	DRY	< DL	< DL	< DL	< DL	< DL	0.003	0.005
Copper mg/l	WET	0.34±0.02	0.08±0.02	0.08±0.01	0.11±0.00	0.12±0.01		
	DRY	0.52±0.03	0.58±0.00	0.58±0.01	0.60±0.02	0.59±0.01	1.0 - 2.0	0.1
Nickel mg/l	WET	0.35±0.01	0.24±0.03	0.13±0.01	0.24±0.05	0.14±0.03		
	DRY	0.42±0.03	0.35±0.03	0.45±0.03	0.61±0.03	0.94±0.05	0.07	0.05
Chromium mg/l	WET	0.04±0.00	0.10±0.01	0.18±0.01	0.24±0.01	0.29±0.01		
	DRY	0.04±0.01	0.03±0.01	0.10±0.01	0.08±0.00	0.06±0.00	0.05	0.05
Zinc mg/l	WET	0.10±0.01	0.13±0.01	0.10±0.01	0.21±0.02	0.33±0.01		
	DRY	0.24±0.00	0.17±0.00	0.16±0.02	0.13±0.01	0.27±0.01	3.0	5.0
Cobalt mg/l	WET	0.40±0.01	0.35±0.01	0.38±0.01	0.37±0.01	0.35±0.01		
	DRY	1.03±0.16	0.76±0.06	0.95±0.06	1.18±0.13	1.28±0.06	0.05	0.05
Iron mg/l	WET	10.57±0.58	13.73±0.18	10.00±0.28	8.93±0.10	8.78±0.13		
	DRY	2.93±0.08	4.11±0.11	3.88±0.10	4.29±0.09	4.22±0.14	0.3	0.3

* *Bolded values are those that are above the recommended limits by WHO* *KEBS = Kenya Bureau of Standards

Table 3. Correlation coefficient matrix for water quality parameters - dry season

	pH	EC	TDS	°C	DO	TURB	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻	Cl ⁻	Mn	Cu	Ni	Cr	Zn	Co	Fe
pH	1.00																
EC	-0.04	1.00															
TDS	-0.22	0.98	1.00														
°C	-0.32	0.96	0.98	1.00													
DO	0.00	0.00	0.13	0.01	1.00												
TURB	-0.77	-0.39	-0.30	-0.16	-0.46	1.00											
NO ₃ ⁻	0.13	0.90	0.89	0.84	0.34	-0.66	1.00										
PO ₄ ³⁻	-0.54	-0.74	-0.67	-0.53	-0.23	0.83	-0.79	1.00									
SO ₄ ²⁻	-0.23	-0.50	-0.51	-0.34	-0.22	0.43	-0.41	0.78	1.00								
Cl ⁻	0.96	-0.13	-0.31	-0.37	-0.09	-0.69	0.06	-0.37	0.03	1.00							
Mn	0.34	0.57	0.59	0.46	0.73	-0.85	0.83	-0.79	-0.52	0.21	1.00						
Cu	0.22	0.62	0.65	0.48	0.52	-0.63	0.67	-0.86	-0.91	-0.02	0.81	1.00					
Ni	0.32	0.87	0.74	0.73	-0.34	-0.46	0.73	-0.77	-0.45	0.26	0.37	0.45	1.00				
Cr	-0.41	0.65	0.78	0.75	0.63	-0.26	0.77	-0.36	-0.22	-0.47	0.70	0.53	0.22	1.00			
Zn	-0.03	0.19	0.06	0.19	-0.98	0.39	-0.14	0.12	0.21	0.07	-0.61	-0.45	0.49	-0.46	1.00		
Co	0.35	0.77	0.64	0.67	-0.21	-0.54	0.78	-0.62	-0.07	0.40	0.44	0.22	0.88	0.30	0.40	1.00	
Fe	0.33	0.55	0.56	0.38	0.45	-0.65	0.58	-0.88	-0.95	0.08	0.75	0.99	0.45	0.39	-0.40	0.18	1.00

Bolded values show significant correlation

Table 4. Correlation coefficient matrix for water quality parameters - wet season

	pH	EC	TDS	°C	DO	TURB	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻	Cl ⁻	Mn	Cu	Ni	Cr	Zn	Co	Fe
pH	1.00																
EC	-0.88	1.00															
TDS	-0.12	0.09	1.00														
°C	-0.42	0.59	0.81	1.00													
DO	-0.55	0.74	0.69	0.98	1.00												
TURB	0.05	-0.19	-0.90	-0.85	-0.77	1.00											
NO ₃ ⁻	0.99	-0.90	-0.21	-0.51	-0.64	0.19	1.00										
PO ₄ ³⁻	0.31	-0.30	-0.83	-0.75	-0.72	0.91	0.44	1.00									
SO ₄ ²⁻	-0.53	0.36	0.89	0.77	0.71	-0.71	-0.58	-0.80	1.00								
Cl ⁻	0.00	-0.03	0.69	0.55	0.41	-0.41	0.01	-0.19	0.61	1.00							
Mn	0.10	-0.40	0.43	0.03	-0.13	-0.02	0.17	0.04	0.45	0.79	1.00						
Cu	-0.51	0.32	-0.70	-0.53	-0.36	0.68	-0.44	0.34	-0.32	-0.71	-0.38	1.00					
Ni	-0.13	0.20	-0.94	-0.62	-0.44	0.76	-0.07	0.62	-0.76	-0.81	-0.66	0.80	1.00				
Cr	-0.32	0.43	0.92	0.97	0.92	-0.93	-0.43	-0.85	0.84	0.57	0.12	-0.60	-0.75	1.00			
Zn	-0.67	0.78	0.62	0.92	0.94	-0.58	-0.71	-0.53	0.73	0.56	0.08	-0.28	-0.42	0.83	1.00		
Co	0.00	-0.15	-0.59	-0.66	-0.55	0.44	0.00	0.13	-0.46	-0.92	-0.52	0.75	0.66	-0.61	-0.67	1.00	
Fe	0.62	-0.55	-0.58	-0.64	-0.69	0.68	0.72	0.91	-0.73	0.07	0.23	-0.07	0.30	-0.69	-0.54	-0.12	1.00

Bolded values show significant correlation

for chromium in water were also reported during the determination of heavy metals health risk index in human consumption of whole fish and water from some selected dams in Katsina state, Nigeria [24].

Cobalt concentration ranged from 0.76 ± 0.06 mg/l to 1.28 ± 0.06 mg/l during the dry season and 0.35 ± 0.01 mg/l to 0.40 ± 0.01 mg/l during the wet season. Seasonal variations showed significant difference with $T_{\text{calculated}} = 7.35 > T_{\text{critical}} = 2.78$ at $P = .05$. The high concentrations of cobalt can be linked to leaching from rocks and soil and alloys from scrap metals that are dumped in the River. Spatial variations were statistically significant, with $F_{\text{calculated}} = 11.89$ and 13.53 during the dry and wet seasons respectively which was greater than $F_{\text{critical}} = 3.49$ at $P = .05$. All the stations recorded cobalt concentrations above the recommended WHO limits of 0.05 mg/l. The high concentrations during the dry season can be attributed to evaporation of water from the river, leading to a lower volume of the river water. High concentration of cobalt during dry season and low concentrations during the wet season were also reported in the study of seasonal variation of metallic contamination of water and sediments in navigation canal and industrial zone south Port Said, Egypt [25].

3.4 Correlation

During the dry season, chloride was strongly correlated to pH ($r = 0.96$) while electrical conductivity was strongly correlated to total dissolved solids, temperature, nitrates, copper, nickel, chromium and cobalt, with medium correlation to manganese and iron. Total dissolved solids were strongly correlated to temperature, nitrates, nickel, cobalt and chromium, with medium correlation to iron and manganese. Nitrate was strongly correlated to manganese, copper, chromium, nickel and cobalt with medium correlation to iron, meaning that these metal compounds mostly occur in nitrate form. Copper showed strong correlation to iron ($r = 0.99$) with medium correlation to chromium ($r = 0.53$) while nickel showed strong correlation to cobalt ($r = 0.88$). During the wet season, pH showed strong correlation with nitrate ($r = 0.99$) indicating a high concentration of nitrate ions from farms as a result of surface run-off during the wet season. There was a strong correlation between temperature and dissolved oxygen ($r = 0.98$), sulphate, chromium and zinc. The correlation between turbidity and phosphates

was high ($r = 0.91$) indicating high concentrations of phosphates being carried into the River during the wet season as a result of surface run-off. Several metals showed a high correlation with turbidity and they include copper, nickel and iron. Phosphate showed a strong correlation with nickel and iron, whereas sulphate showed strong correlation to chromium and zinc, which is a strong indication that these metals exist in the form of phosphates and sulphates respectively.

4. CONCLUSION

Turbidity, phosphates, lead, nickel, chromium, cobalt and iron were the parameters that were above the WHO recommend levels, mainly as a result of surface run-off during wet season as a result of poor farming practices which lead to increased soil erosion, as top fertile soil rich in nutrients and minerals is carried by surface run-off and dumped into the river, leading to an increase in the concentration of the above parameters during the wet season. These high levels pose a threat to terrestrial and aquatic life that depend on water from the river and imposes high treatment cost to downstream users. Land use along river Sio has resulted to change in the concentration of the above parameters during wet season according to spatial variation tests using one way ANOVA.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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