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Physicochemical Parameters and Effects of Zinc and Copper on Aquatic Biota of Elechi Creek in Port Harcourt, Nigeria

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Abstract:
Physicochemical parameters and effects of zinc and copper on the aquatic biota of Elechi Creek in Port Harcourt, Nigeria were studied experimentally for a period of six (6) months in water, sediment and plankton. The study covers three (3) months of dry and wet seasons in three (3) different locations. Mathematical models were developed by the application of the principle of regression analysis to study the relationship that exists between the metals in water, sediment and plankton. The model results were compared with the experimental results for each of the metals in water, sediment and plankton and the results showed reasonable agreement with slight deviations as follows: for Zinc (Zn) -0.07 to 0.04, -0.04 to 0.02 and -0.14 to 0.1, for Copper (Cu) -0.05 to 0.08, -0.02 to 0.01 and -0.05 to 0.01 in water, sediment and plankton respectively. Concentration of heavy metal in plankton, sediment and water varied seasonally. The results indicated that changing water quality of Elechi creek affected the aquatic biota in terms of diversity and abundance.

Keywords: Physicochemical parameters, zinc, copper, water, plankton, mathematical modelling and sediment

1.0 INTRODUCTION

Heavy metals are inorganic elements essential for plant growth, in trace or very minute quantities, toxic and poisonous in relatively higher concentrations, biologically non-degradable but easily assimilable and bio-accumulated in the protoplasm of aquatic organisms. Metals are natural trace components of the aquatic environment, but their levels have been increased due to industrial wastes, geochemical structure, agricultural and mining activities. There are certain heavy metals such as As, Cd, Cu, Pb, Ni and Zn are common pollutants and came from different natural and anthropogenic sources (Yahya et al., 2018). Heavy metals are of high ecological significance since they are not removed from water as a result of self-purification, but accumulate in reservoirs and enter the food chain (Loska and Wiechuła, 2003). The elevation of metal levels in a reservoir is shown mainly by an increase of their concentrations in the bottom sediment. Accordingly, sediments represent one of the ultimate sinks for heavy metals discharged into the environment [Loska and Wiechuła, 2003; Gibbs, 1973]. Heavy metals enter the aquatic ecosystem from both natural and anthropogenic sources. Entry may be as a result of direct discharges into both fresh and marine ecosystems or through indirect routes such as dry and wet deposition and land run-off (Bineyet al., 1994). Once in the aquatic environment, metals are partitioned among the various aquatic environmental compartments (water, suspended solids, sediments and biota), the metal in the aquatic environment may occur in dissolved, particulates or complex form. The main processes governing distribution and partitioning are dilution, dispersion, sedimentation and adsorption/desorption, nonetheless some chemical processes could also occur. Thus speciation under the various soluble forms is regulated by the instability consists of the various complexes and by the physico-chemical properties of the water (pH, dissolved ions, Eh and temperature Namieśnik and Rabajczyk, (2010). Soils and sediments contain some toxic heavy metals bound within the structural lattice of the crystalline minerals as primary constituent. Metals in this form are un-reactive and only slowly become available over geologic times as the result of natural mineral weathering. The metals fixed within the lattice of minerals are the dominant constituents. Between the readily available and unavailable forms of metals in sediments are a number of chemical forms which are potentially available. Metals in these potentially available forms may possibly be mobilized to more readily bio-available forms as a consequence of relatively mild physico-chemical changes in sediments and surface waters (Förstner, 1987).

The occurrence of these metals contaminants especially in excess of natural levels in recent times has become a problem of increasing concern. This is because its accumulation in the sediments, water and tissues of aquatic microbiota (plants and animals) affect their productivity (Yan *et al.*, 2007). The accumulation of heavy metals in the sediments and water affect the physicochemical properties of the aquatic environment and so alter the entire physiological and metabolic processes of the aquatic biota. He *et al.* (2005) disclosed that in the aquatic ecosystems, heavy metals have received considerable attention due to their toxicity and accumulation in biota. Aquatic organisms have been used in comparative monitoring of pollution effects in different systems and to locate sources of toxicants (Duffus, 2002). Bio-monitoring approach has proved to promising as a reliable means of quantifying biological effects of complex effluents (Bradl, 2002). Although a large number of aquatic organisms have been used for assessment, many other researchers have recognized the importance of algae as indicator in assessment and evaluation of pollution (Arruti*et al.*, 2010). Typical results of human activities proved to be elevated levels of heavy metals present in fresh water, and among these microelements lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr) are most specific (Neal *et al*., 2001). This study will be conducted to determine the accumulation of heavy metals in water and plankton (phytoplankton and zooplankton) of Elechi Creek.

2.0 MATERIALS AND METHODS

The study area from which samples were obtained is the Elechi Creek, close to the Eagle Island, extending to the Iloabuchi Street water bank in Diobu, Port Harcourt. The Eagle Island is located on the South-West of Port Harcourt and bounded on the North by the Rivers State University of Science and Technology in Nkpolu-Oroworukwo area of Diobu. The Elechi creek is a brackish water system influenced by tidal fluxes. It has mangrove vegetation. The configuration of the creek basin, which widens in some regions and narrows in some other areas, restricts the tidal flow height close to the Nkpolu-Oroworukwo area of Diobu.
The Elechi creek water is important as it serves as a means of transportation for humans, fell logs of wood and building materials. The surrounding terrestrial environment is marked with various human activities such as saw milling of timber, waste disposal and frequent defecation on the banks of the creek. Pig breeding on a free-range basis, is also practiced in the area. (Obire, et al., 2003).

2.1 Water Sampling and Analysis

Water samples were collected from the water surface at the various sampling stations using one-litre plastic containers Merrett, (2000). The water samples collected were kept in an acid rinsed polyethylene bottles and later filtered through the 0.45µm membrane filter and acidified with concentrated nitric acid to a pH of 2 Tahir *et al.,* (2008). The acidified samples were kept for determination of heavy metals using Buck Scientific Atomic Absorption/Emission Spectrophotometry 200A. It was also used for the determination of some physicochemical parameters of water.

2.2 Sediment Sampling and Analysis

About 4-5cm of the top of sediment samples was collected from each of the three stations which are approximately 500m apart using grab sampler. At least l00g of the sediment samples was collected in glass containers as recommended by ASTM (1990) Guide for collection, storage, and characterization for toxicological testing and transported in ice chest at 4°C to the laboratory for preparation, treatment and analysis.
In the laboratory, representative portions were oven dried at 200°C to constant weight, crushed and passed through a 2mm mesh sieve to do away with coarse materials. Later, about 2g of the sample was weighed with the triple beam balance and turned into the evaporating dish. 25ml of distilled water was added followed by 0.5ml of nitric acid ($HN0_3$) and 5ml of hydrochloric acid (HCl) and thoroughly digested for about 45m on the steam bath to release the total metal content from the sediment into solution (Loring and Rantala, 1992, APHA, 1985). The samples were extracted by filtering with Whatman No. 1 filter paper into 50ml volumetric flasks and the filtrate diluted with distilled water to the 50ml mark and poured into the vial bottle which was kept in the freezer until it was sent to the laboratory for determination of heavy metals using Buck Scientific Atomic Absorption/Emission Spectrophotometry 200A.

2.3 Biota Sampling and Analysis

Biota (plankton) samples were collected by throwing plankton net (25 µm) five minutes duration. Samples were collected by horizontal dragging of the net in water using speed boat in each of the station at 500m apart for 10 minutes. Collected samples were transferred into plastic samples bottles and were preserved in 4% formalin solution (Ezra and Nwankwo, 2001, Trivedi *et al.,* 2003). The plankton samples collected were also used for heavy metal determination. The samples were preserved for some time and later sent to the laboratory for enumeration and identification.

2.4 Laboratory Methods

2.4.1 Plankton Enumeration and Identification

The concentrated plankton sample were thoroughly mixed and 1ml of the sample was drawn with a dropping pipette into a Sedgwick Kafter counting chamber and was examined using an inverted microscope (X100) or the electrical Nikon biological microscope or digital microscope. Plankton were identified and the total number per species were recorded using keys and checklist of Neal (2003), Thorp and Vukovic (2011). The samples collected for plankton analysis were filtered through ash-less filter paper with concentrated plankton left in laboratory for some time for small evaporation of water. Age-weight was determined following Tahir *et al;* (2008). Material was then dried in oven at 90°C for 24 hours and its dry weight was noted. The material was then kept at 550°C for 4 hours and then cooled down. It was digested at 80°C by adding 20 ml of 1.5N HC1, filtered into 100 ml test tubes, 100 ml distilled water was added and samples were analysed with a Hitachi Z 8200 polarized Zeeman AAS (Atomic Absorption Spectrophotometer) at the Institute of Pollution Studies, Rivers State University Port Harcourt and soil science laboratory respectively.

2.4.2 Analysis of Data

The estimated count of plankton was observed per litre and subjected to the formula modified by Bradl, (2002).

$$\text{Density or plankton (ind/ml)} = T\left(\frac{100}{AN}\times\frac{Volume\ of\ concentration}{volume\ of\ sample}\right)i$$

where, T = total number of plankton counted, A = Area of grid in mm^2, *i*- number of grids employed, 100 = area of counting chamber in mm (Tang *et al.,*2010).

2.5 Physicochemical Parameters

The various water parameters were studied following the normal procedures as recorded in the standard method.

2.5.1 Temperature

The water temperate was measured using (in-situ) mercury in bulbs thermometers at the various stations.

2.5.2 pH

The pH values of the water and sediment samples were determined in the laboratory using an EIL Model 720 pH meter or model EC10 each. The pH was determined by simply dipping the electrode into a 200ml of water that had been stirred and the reading was subsequently read off the meter.

2.5.3 Dissolved Oxygen

Water samples were collected from each station with 70ml DO bottles followed by the addition of each Winkler Solution I (manganese II tetraoxosulphate IV monohydrate and II (sodium hydroxide and sodium iodide) to fix it in the sample. Also, 0.5ml of concentrated tetraoxosulphate VI acid (H_2S0_4) was added to liberate the iodine equivalent of dissolved oxygen in the titration with the thiosulphate.

2.5.4 Electrical Conductivity

This will be determined from the water sample using Griffin Conductance Bridge. Electrical conductivity will be measured or expressed as µs/cm.

2.5.5 Biological Oxygen Demand (BOD)

Samples for this variable were collected from the respective stations with 70ml bottles. The samples were stored 5 days before fixing and titration. After this Winkler I and II solutions were added to the samples followed by 0.5ml of concentrated H_2S0_4. The bottles were inverted after which 25ml of the samples were transferred into 100ml flask and 2 drops of starch were added.

2.6 Mathematical Models

Using regression analysis as a statistical modelling approach in the determination of heavy metal accumulation in water, sediment and plankton, the following representative models for zinc and copper were obtained as:

For zinc

$$Sznw = \left(\frac{n\sum st - (\sum s)(\sum t)}{n\sum t^2 - (\sum t)^2}\right)_{znw}^{t+} \left(\frac{\sum s}{n} - \frac{n\sum st - (\sum s)(\sum t)}{n(\sum t^2) - (\sum t)^2}\frac{\sum t}{n}\right)_{znw} \quad (1)$$

$$Szns = \left(\frac{n\sum st - (\sum s)(\sum t)}{n\sum t^2 - (\sum t)^2}\right)_{zns}^{t+} \left(\frac{\sum s}{n} - \frac{n\sum st - (\sum s)(\sum t)}{n(\sum t^2) - (\sum t)^2}\frac{\sum t}{n}\right)_{zns} \quad (2)$$

$$Sznp = \left(\frac{n\sum st - (\sum s)(\sum t)}{n\sum t^2 - (\sum t)^2}\right)_{znp}^{t+} \left(\frac{\sum s}{n} - \frac{n\sum st - (\sum s)(\sum t)}{n(\sum t^2) - (\sum t)^2}\frac{\sum t}{n}\right)_{znp} \quad (3)$$

For copper

$$Scuw = \left(\frac{n\sum st - (\sum s)(\sum t)}{n\sum t^2 - (\sum t)^2}\right)_{cuw}^{t+} \left(\frac{\sum s}{n} - \frac{n\sum st - (\sum s)(\sum t)}{n(\sum t^2) - (\sum t)^2}\frac{\sum t}{n}\right)_{cuw} \quad (4)$$

$$Scus = \left(\frac{n\sum st - (\sum s)(\sum t)}{n\sum t^2 - (\sum t)^2}\right)_{cus}^{t+} \left(\frac{\sum s}{n} - \frac{n\sum st - (\sum s)(\sum t)}{n(\sum t^2) - (\sum t)^2}\frac{\sum t}{n}\right)_{cus} \quad (5)$$

$$Scup = \left(\frac{n\sum st - (\sum s)(\sum t)}{n\sum t^2 - (\sum t)^2}\right)_{cup}^{t+} \left(\frac{\sum s}{n} - \frac{n\sum st - (\sum s)(\sum t)}{n(\sum t^2) - (\sum t)^2}\frac{\sum t}{n}\right)_{cup} \quad (6)$$

3.0 RESULTS AND DISCUSSION

3.1 Physicochemical Parameters of Water

The results of the parameters studied, namely temperature, pH, electrical conductivity, dissolved oxygen (DO), biological oxygen demand (BOD), chemical oxygen demand (COD) and total hydro-carbon compound (THC) are presented.

3.1.1 Temperature

The temperature value recorded ranged from 25 -28°C with the lowest mean (26.07 ± 0.83)^{0}C observed in station 2 and the highest (26. 22 ± 1.09^{0}C) observed in station 1. The lowest monthly temperature (25 .40 ± 0.10°C) was observed in January while the highest (27 .30 ± 0.61)^{0}C was observed in September. Seasonally, temperature values were higher in the wet season (26.53 ± 0.84^{0}C) than dry season (25. 73 ± 0.58^{0}C) though there was no significant difference (Fig. 1 and Fig. 2).

3.1.2 pH:

pH value ranged from 5.90 -7.00 with the overall mean, 6.33 ± 0.31. The lowest pH (6.18 + 0.25) was recorded in station 1 while the highest (6.50 ± 0.42) was observed in station 2. The lowest monthly pH (6.03 ± 0.06) was observed in August while the highest value (6.60 ± 0.17) was observed in February (Fig. 1 and Fig.2).

3.1.3 Electrical Conductivity(EC)

Electrical Conductivity (EC) ranged from 13200 - 24500µs/cm with the overall mean of 20.288.89 ± 3824. 363 µs/cm. The lowest spatial value (15.216, 67 ± 13. 65.89 µs/cm while the highest spatial mean (23266.67 ± 708.99 µs/cm. The lowest monthly value (19233.33 ± 5278. 66 µs/cm) was observed in January while the highest value (21400 ± 3811.82 *v* s/cm). EC shows significant difference with wet season value (209988.89 + 3628.57 µs/cm) higher than the dry season value (19588. 89 ±410014 µs/cm) (Fig. 1 and Fig. 2).

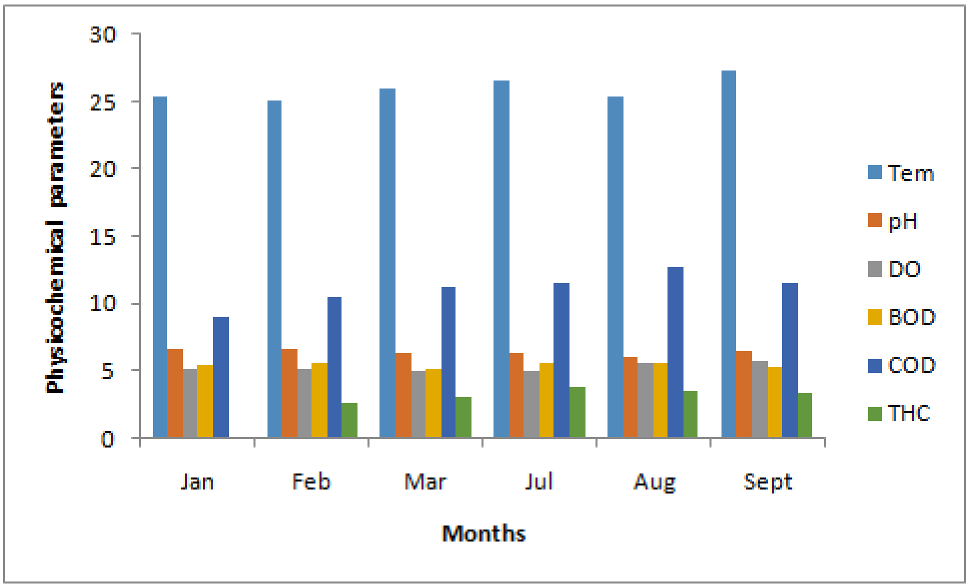

Figure.1. Mean Values of Physicochemical Parameters of Water

3.1.4 Dissolved Oxygen (DO)

The DO values, range from 3.20 - 7.3mg/l with the overall mean of 5.13 ± 12mg/l. The lowest spatial mean value (4.47 ± l.04mg/l) was observed in station 3 while the highest value (6.37 ± 0.5 mg/1) was recorded in station 2. The lowest monthly value (4.87 ± 1.65mg/l) was observed in March while the highest mean value 5.67± 0.58mg/l was observed in September. Seasonally, wet season value was higher than the dry season value (Fig. 1 and Fig. 2).

3.1.5Biological Oxygen Demand (BOD): Biological Oxygen Demand (BOD) ranged from 1.40 -10.0mgl/l with the overall mean of 6.30 ± 2.38mg/l. Spatially, station 3 (3.43 ± 1.35mg/l) recorded the lowest BOD while the highest value (6.98 ± 0.09mg/l) was recorded in station 2. The lowest monthly value (5.57 + 2.93mg/l) was observed in February while the highest (7.33 ± 2.52mg/l) was recorded in station 3. Seasonally, wet season value (6.89 ± 2.21mg/l) was higher than the dry reason value (5.71 ± 2.53mg/l) (Fig. 1 and Fig. 2).

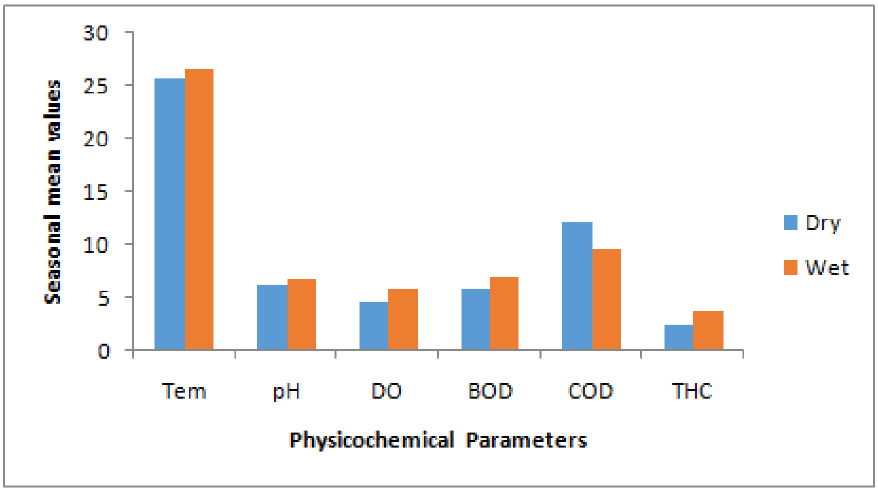

Figure.2. Seasonal Mean Values of Physicochemical Parameters in Water

3.1.6 Chemical Oxygen Demand (COD)

COD values ranged from 2.20 - 13.60mg/I with the overall mean value of 10.82 ± 3.10mg/l. Spatially, station 3 recorded the lowest COD (8.10 ± 4.22mg/l) while station I recorded the highest value (12.40 ± 0.85mg/l). The lowest monthly value (9.07 ± 3.83mg/l) was observed in January while the highest value (12.67 ± 0.58mg/I) was observed in August. Seasonally, wet season value (12.11 ± 1.05) recorded higher value than dry season (9.53 ± 3.95mg/l) with significant difference (Fig. 1 and Fig. 2).

3.1.7 Total Hydrocarbon Compound (THC)

Total hydrocarbon compound observed ranged from 0 -5mg/l with the overall mean value of 3.04 ± 1.79. The lowest spatial value (1.85 ± 1.16mg/l) was observed in station 1 while the highest value (3.63 ± 1.92mg/I) was observed in station 2 and 3. The lowest temporal value of THC was observed in January while the highest value (4.00 ± l.00mg/1) was recorded in July and August. Seasonally, wet season value (3.67 + 1.00) was higher than the dry season value (2.40 ± 2.20mg/l) (Fig. 1 and Fig. 2).

3.2 Heavy Metals in Water

Table.1. Spatial Mean Values of Heavy Metals in Water

Metal/Station	Zn	Cu
1	0.19±0.10	0. 101±0.12
2	0.14±0.12	0.07±0.04
3	0.16±0.ll	0.08±0.06
Overall mean	0.17±0.13	0.091±0.08

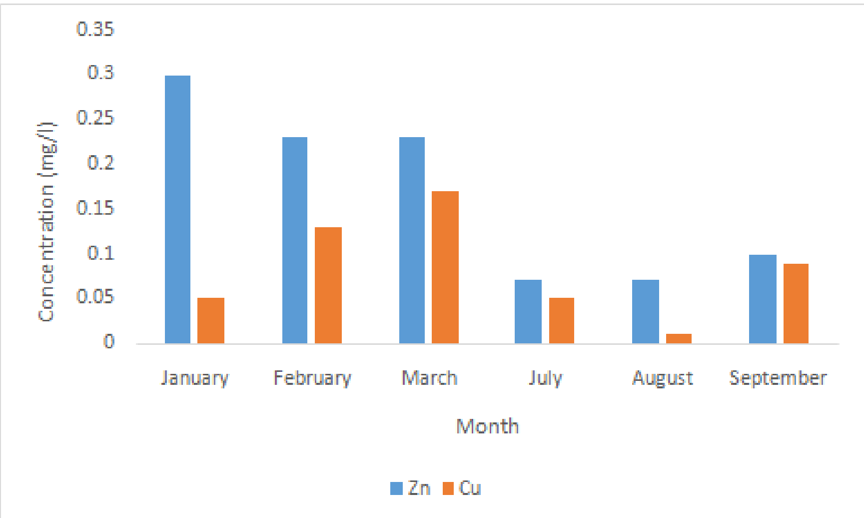

Figure.3. Mean Values of Heavy Metals in Water

Zinc is lowest in August (0.07 ± 0.10mg/l) and July but highest in January. Copper is lowest (0.01 ± 0.00lmg/1) in August but highest (0.17 ±0.10mg/l) in March. Seasonally, only zinc did not show significant difference at p ≤ 0.05. In terms of station, zinc in station 2 < 3 < 1 while in copper, station 2 < 3 <1.

3.3 Heavy Metals in Sediment

Table 2: Spatial Mean Values of Heavy Metals in Sediment

Station	Zn	Cu
1	0.17±0.10	0.11±0.08
2	0.11±0.06	0.06±10.02
3	0.13±0.10	0.05±0.02
Overall Mean	0.14±0.10	0.07±0.02

In. terms of station, zinc in station 2 < 3 < 1 while in copper, station3 < 2 <1.
The heavy metal concentration in the water is higher than the sediment but lower than the plankton.

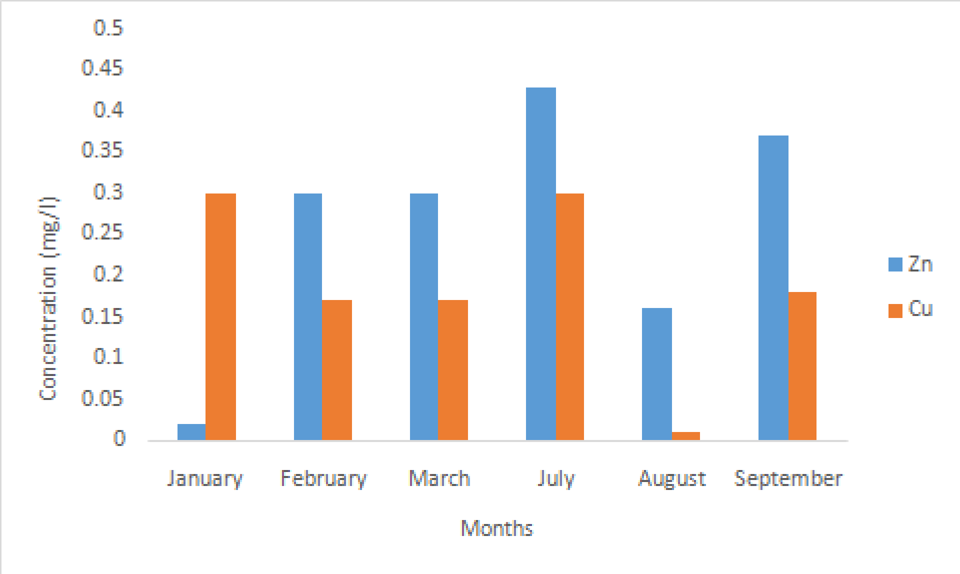

Figure.4. Mean Values of Heavy Metals in Sediment

Concentration of Zinc was lowest in August and September (0.02 + 0.00lmg/1) but highest in January (0.11 ± 0.0lmg/1). Seasonally, only lead did not show significant difference whereas others showed significant difference between seasons.

3.4 Heavy Metal Accumulation in Plankton

The order of heavy metal concentrations in the plankton are zinc (0.24 ± 0.21 mg/1), and copper (0.10 ± 0.18mg/l). It is therefore in the order copper < zinc (Cu< Zn) Spatially, Zinc concentration was lowest (0.18 ± 0.llmg/1 (in station 2 while the concentration was lowest (0.18 ± 0.llmg/1 (in station 2 while the Copper had the lowest value (0.07 ± 0.0lmg/1) in station 2, and the lowest value (0.16 ± 0.12mg/l) in station 1 as a result of geographical variation.

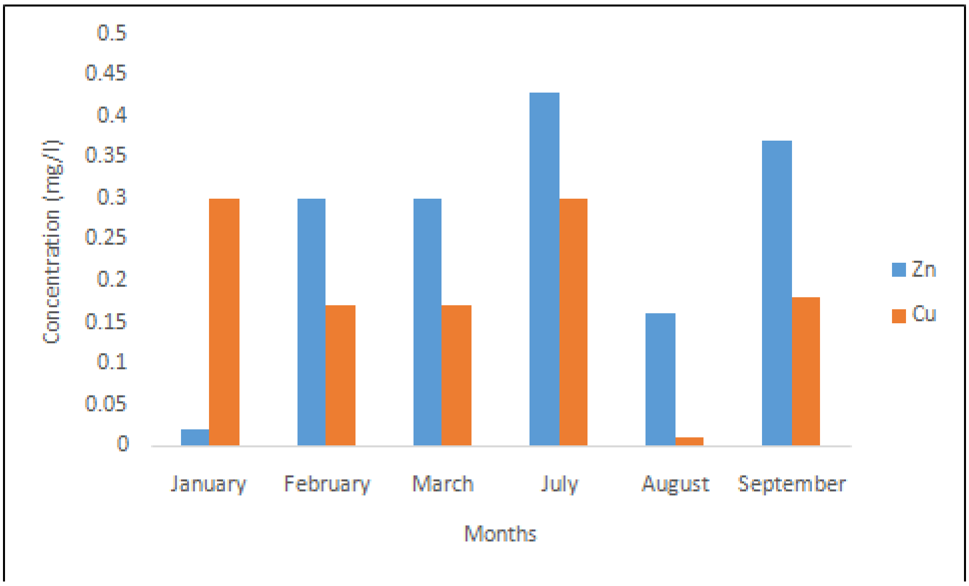

Figure.5. Mean Values of Heavy Metals in Plankton

Concentration of Zinc was lowest (0.08 ± 0.002mg/l) in August and September but highest (0.50 ± 0.30mg/l) in January. Copper was lowest (0.04 ± 0.001 mg/1) in September but highest (0.30 ± 0.20mg/l) in January.

Table.3. Spatial Mean Values of Heavy Metals in Plankton

Station	Zn	Cu
1	0.22±0.12	0.16±10. 10
2	0.18±0.11	0.07±0.01
3	0.31±0.10	0.08±l0.01
OverallMean	0.24±0.21	0.10±10.18

3.5 Model Validation

Table.4. Comparison between Experimental and Model results of Concentration of Zinc in Water

Experiments $_{znw}$	Models $_{znw}$	Error
0.30	0.29	0.01
0.23	0.24	–0.01
0.23	0.19	0.04
0.07	0.14	–0.07
0.07	0.10	–0.03
0.10	0.05	–0.05

Table.5. Comparison between Experimental and Model results of Concentration of Zinc in Sediment

Experiment$_{zns}$	Models $_{zns}$	Error
0.23	0.23	0.00
0.20	0.19	0.01
0.17	0.15	0.02
0.07	0.11	–0.04
0.07	0.07	0.00
0.05	0.03	0.02

Table. 6. Comparison between Experimental and Model results of Concentration of Zinc in Plankton

Experiments$_{znp}$	Models$_{znp}$	Error
0.50	0.40	0.10
0.20	0.34	-0.14
0.23	0.27	-0.04
0.33	0.20	0.13
0.08	0.14	-0.06
0.08	0.07	0.01

Table.7. Comparison between Experimental and Model results of Concentration of Copper in Water.

Experiments $_{cuw}$.	Models $_{cuw}$.	Error
0.05	0.10	–0.05
0.13	0.10	0.03
0.17 ^{s}	0.09	0.08
0.05	0.08	–0.03
0.01	0.07	0.06
0.09	0.06	0.03

Table.8. Comparison between Experimental and Model results of Concentration of Copper in Sediment

Experiments $_{cus}$	Models$_{cus}$	Error
0.11	0.13	0.02
0.09	0.10	0.01
0.15	0.08	0.07
0.04	0.06	–0.02
0.02	0.04	–0.02
0.02	0.02	0.00

Table .9. Comparison between Experimental and Model results of Concentration of Copper in Plankton

Experiments $_{cup}$	Models $_{cup}$	Error
0.18	0.17	0.01
0.12	0.14	–0.02 -
0.17	0.12	0.05
0.04	0.09	–0.05
0.06	0.06	0.00
0.04	0.03	0.01

4.0. CONCLUSION

This research was carried out to ascertain the plankton community of Elechi Creek in relation to physicochemical parameters and heavy metals such as zinc and copper. From the research, it was observed that the water temperature of the creek varied with station and season due to the difference in seasonal conditions, pH values were purely acidic and showed no significant difference both in season and station, Electrical conductivity and dissolved oxygen did not vary with season but vary with station, Biological oxygen demand, chemical oxygen demand and total hydrocarbon content showed significant difference with season and station, heavy metal accumulation in plankton was higher than that of water and sediment, and finally, zinc did not show significant difference with seasons.

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