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Assessment of Heavy Metal Concentrations on the Iwofe and Choba Axis of the New Calabar River, Niger Delta, Nigeria

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ABSTRACT

Heavy metals pose myriads of risk to humans and animals, hence it is necessary to continuously monitor their concentrations in the environment. This research was carried out to evaluate the heavy metal concentrations of the new Calabar River, between September to December 2020. Surface water samples were collected from four stations (STN1, STN2, STN3 and STN4) along the Choba and Iwofe axes of the river. Heavy metal analysis was by Atomic Absorption Spectrophotometry. The result of the study showed variation in heavy metals concentration (mg/l) across the stations studied. The concentration of the metals (mg/l) was as follows: Pb (0.03 ± 0.01– 1.55 ± 0.25); Cr (<0.01 – 0.07 ± 10); Cu (<0.01 – 0.19 ± 0.02); Ni (<0.01 – 0.03 ± 0.01); Zn (0.37 ± 0.13) and Cd (<0.01 – 0.83). Analysis of variance indicated that variation in the concentrations of Pb and Cr were not significantly different ($p>0.05$) but variation in the concentrations of Cu, Ni, Zn and Cd were significantly different ($p<0.05$) between the stations examined. Observations showed that metal levels were generally higher at station STN3 followed by station STN2 compared to other stations. Site discrimination using principal component analysis clearly distinguished stations of Choba and Iwofe axes based on their heavy metal concentrations. The study concluded elevated metal concentrations around ST3 of Iwofe axis of the New Calabar River but isolation of each station within the creek indicated dissimilarity in the water quality relative to heavy metal contamination. This was traced to anthropogenic inputs at the different stations studied.

Keywords: Heavy metals; Choba; Iwofe; Niger Delta.

Introduction

The term "heavy metal" is commonly used to refer to metals and metalloids associated with environmental pollution, toxicity and adverse effects on biota (Varol, 2011). They are recognized as a group of pollutants with high ecological significance because they are not removed from water via self-purification (Ghrefat and Yusuf, 2006). Heavy metals discharged into the environment rapidly associates with particulates and ultimately settles in bottom sediments of water bodies either through discharge or surface run off (Makinde *et al.*, 2015). Heavy metal contamination in the aquatic environment is a major challenge with regards to industrialization in view of the fact that industrial and domestic wastes containing such pollutants are regularly channeled into nearby water bodies (Moslen, 2017). Such heavy metals in most cases end up concentrating and bioaccumulating in tissues of aquatic organisms as reported by some researchers (Moslen *et al*, 2018; Moslen and Miebaka 2018, Moslen and Adiela, 2020; Moslen *et al*., 2020). Public safety and assurance must then be ensured via regular monitoring, detection and control of heavy metal contamination and pollution particularly in the aquatic environment. Heavy metals can accumulate in suspended particulates and sediments, released back into aquatic systems under favourable conditions, enter the food web, and cause health problems (da Silva *et al.,* 2015). Contamination of heavy metals in the aquatic environment has attracted global attention owing to its abundance, persistence and environmental toxicity (Islam *et al*., 2015). This calls for continuous assessment and monitoring of the metal contamination in our environment, particularly the aquatic ecosystem. Some researchers have reported low heavy metal concentration in the surface water bodies of the Niger Dela, Nigeria, among which are Obire *et al*. (2003) on Elechi Creek, Chindah and Braide (2004) on lower Bonny River, Omoigberale and Ogbeibu (2005) on Osse River, Southern Nigeria. The New Calabar River is increasingly receiving diverse types of wastes ranging from human waste from informal settlements, industrial wastes (liquid effluence and solids waste), agrochemicals, domestic wastes, run-offs and other wastes. These wastes come from Choba and its environs as well as the industries sited around the Iwofe axis of the river. This research further sought to assess the concentration of some heavy metals on the Choba and Iwofe axes of the New Calabar River considering wastes from anthropogenic inputs.

Materials and Methods

Study Area

The New Calabar River is located within the Niger Delta in Nigeria (Fig. 1) Nzeako *et al*. (2014). It is a low lying deltaic river which rises at approximately latitude 5°10'N and longitudes 6°50'E near Elele-Alimini and flows southward for roughly 150km before its discharge into the Atlantic ocean at about latitudes 4°20'N and longitudes 7°00'E. It occupies a low relief region, ranging from 0-50m above sea level at the low zone, to 50-100m above sea level at its source. The soil of the river basin consists of clays, silt and sand with high organic matter. The river is unidirectional in the upper reach and tidal in the lower reach. Its upstream reach is fresh water with tropical lowland, dense rainforest through secondary forest/farmland vegetation. The downstream reach is however brackish and consist of mangrove swamp forest.

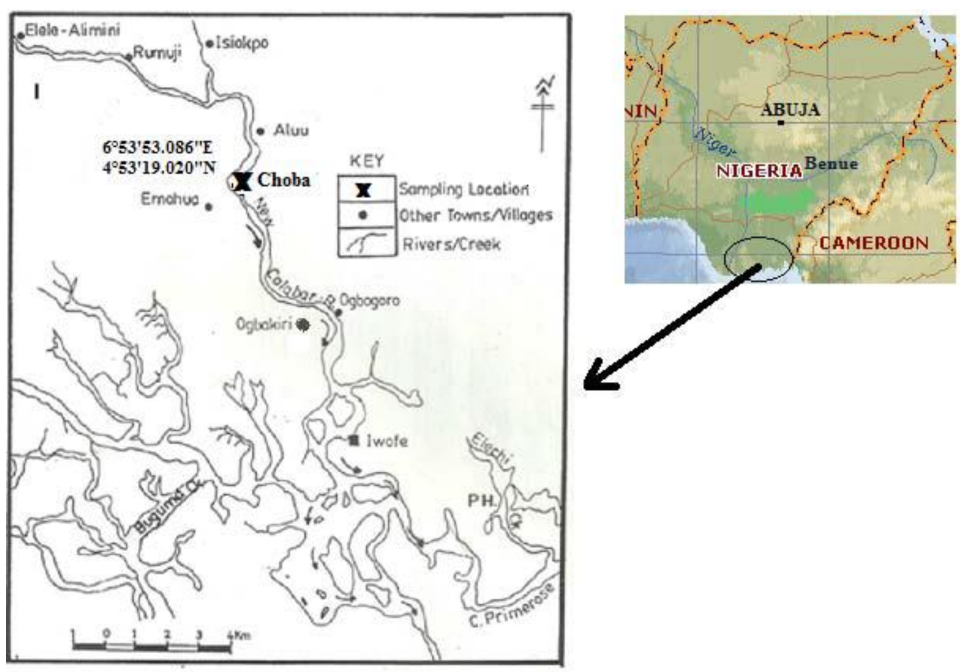

Fig. 1: Map of Study location along the New Calabar River (Source: Nzeako *et al*., **2014)**

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Sample Collection

A total of four sampling stations were established along the upper reaches of the river during this study. Two of the stations were at the Choba axis while the other two were located at Iwofe. Samples were collected monthly for four months (September to December 2020). Samples were collected in pre-washed one litre plastic containers, preserved in ice chests and transported to the laboratory for analysis.

Laboratory Analysis of Heavy Metals in Water

50ml of sample was measured and transferred into a 250ml volumetric flask. 3ml of nitric acid was added to the samples in the flask and transferred to the fume hood. The solution was heated for about 15 to 20 minutes with a hot plate to bring the metals into solution. It was removed from the hot plate and allow to cool for 5 minutes. The solution was filtered with Wartman (41) filter paper into a 50ml volumetric flask and made up to the mark with distilled water. The solution was transferred into 100ml plastic tubes for atomic absorption spectrophotometric (AAS) analysis.

Statistical Analysis

Data collected from the heavy metal analysis were subjected to Analysis of variance (ANOVA) using Minitab while past software was used for principal component analysis.

Results

Concentration of Heavy Metals

The summary of heavy metal concentrations in the study area is presented in Table 1 while the spatial and temporal variations are expressed in Fig 2a – 2g. The mean concentration of Pb ranged from 0.03±0.01 - 1.55±0.25 mg/l while the mean concentration of chromium varied from 0.01±0.01 - 0.07±0.10 mg/l but the variation in the level of these metals was not significantly different ($p>0.05$) between the stations assessed. The concentrations of other heavy metals indicated as follows: Cu (0.00±0.00 - 0.09±0.03mg/l); Ni (0.00±0.00 - 0.03±0.01 mg/l); Zn (0.37±0.13 - 2.31±0.15 mg/l) and Cd (0.00±0.00 - 0.83±0.26 mg/l). The variation observed in the concentrations of Cu, Ni, Zn and Cd were significantly different ($p<0.001$) between the stations examined but none of the heavy metals examined showed significant difference ($p>0.05$) between the months of study. The mean heavy metal concentrations during the study was generally in the order of Zn>Pb>Cd>Cu>Cr>Ni.

Table 1: Spatial variation of heavy metals in the study area

Heavy Metals (mg/l)	Station				P-value
	Station 1	Station 2	Station 3	Station 4	
Pb	0.04±0.04^{a}	0.03±0.01^{a}	1.55±0.25^{a}	0.76±0.49^{a}	0.044
Cr	0.05±0.06^{a}	0.01±0.01^{a}	0.07±0.10^{a}	0.01±0.01^{a}	0.342
Cu	0.09±0.03^{b}	0.02±0.01^{c}	0.19±0.02^{a}	0.00±0.00^{c}	0.000
Ni	0.01±0.01^{b}	0.00±0.00^{b}	0.03±0.01^{a}	0.00±0.00^{b}	0.000
Zn	2.08±0.29^{a}	1.38±0.12^{b}	2.31±0.15^{a}	0.37±0.13^{c}	0.000
Cd	0.83±0.26^{a}	0.01±0.00^{a}	0.04±0.03^{b}	0.00±0.00^{b}	0.000

Mean with similar superscript in the same row shows no significant difference ($P>0.05$) while mean with dissimilar superscript in the same row shows significant difference ($P<0.05$)

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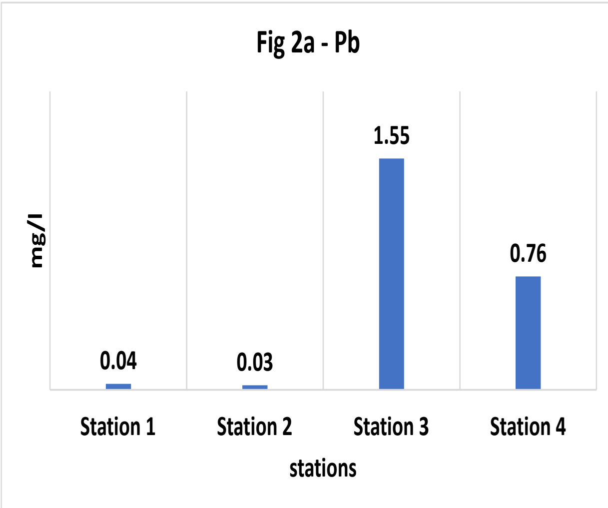

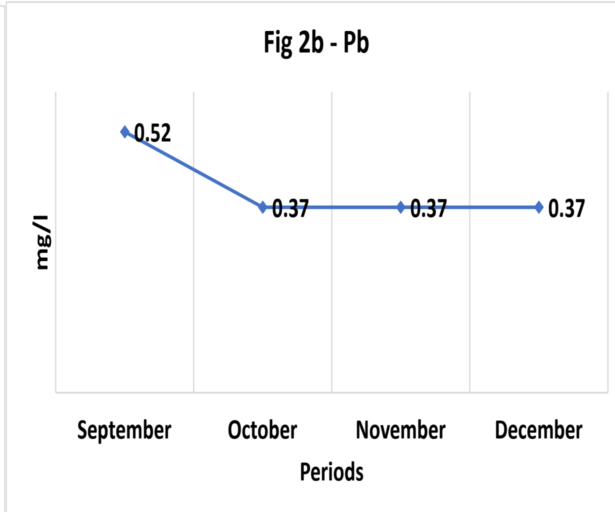

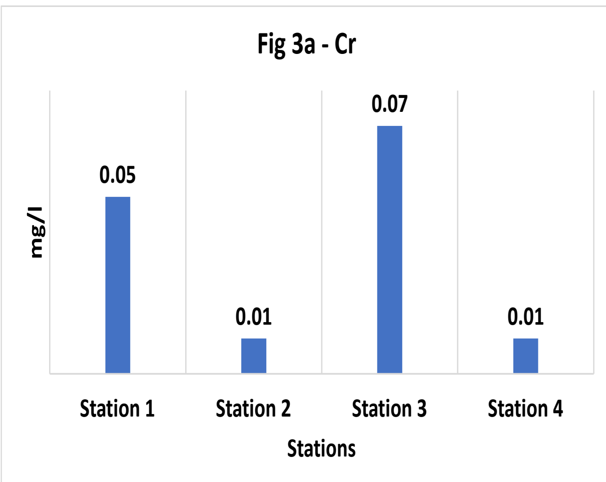

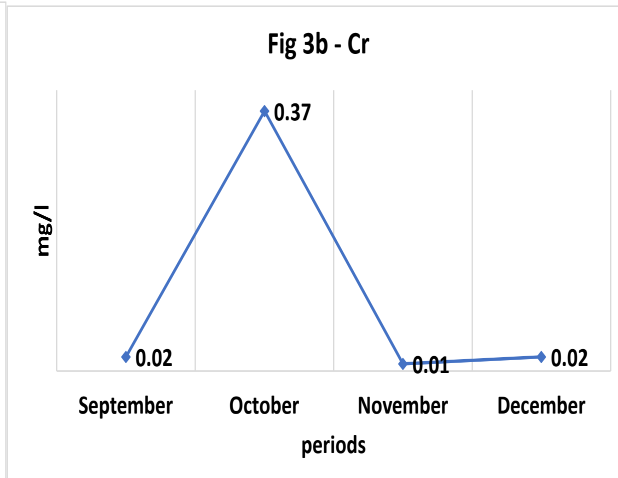

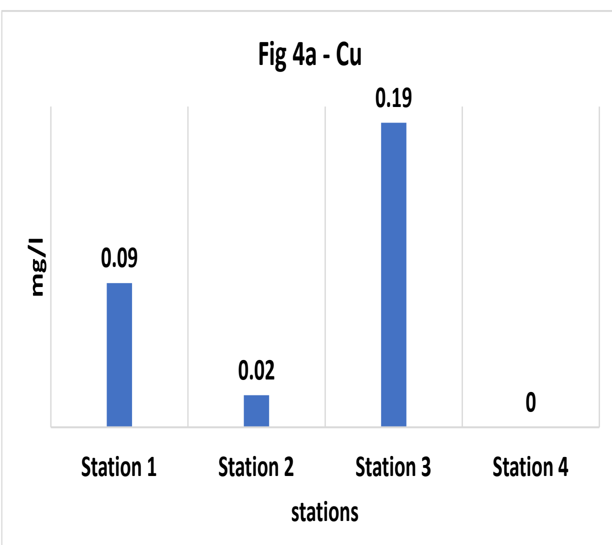

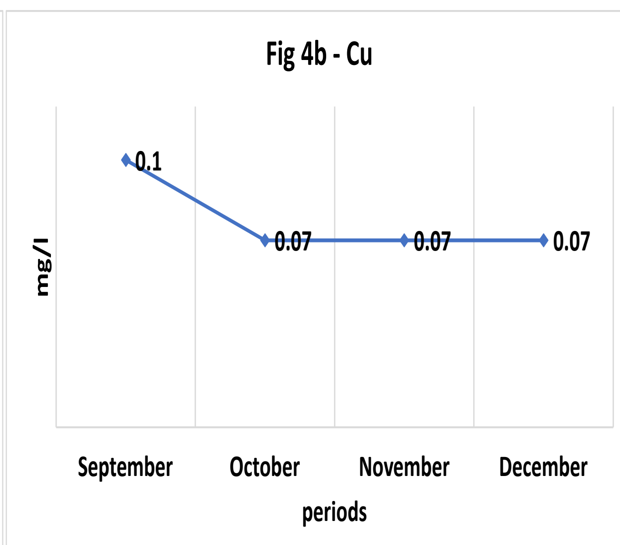

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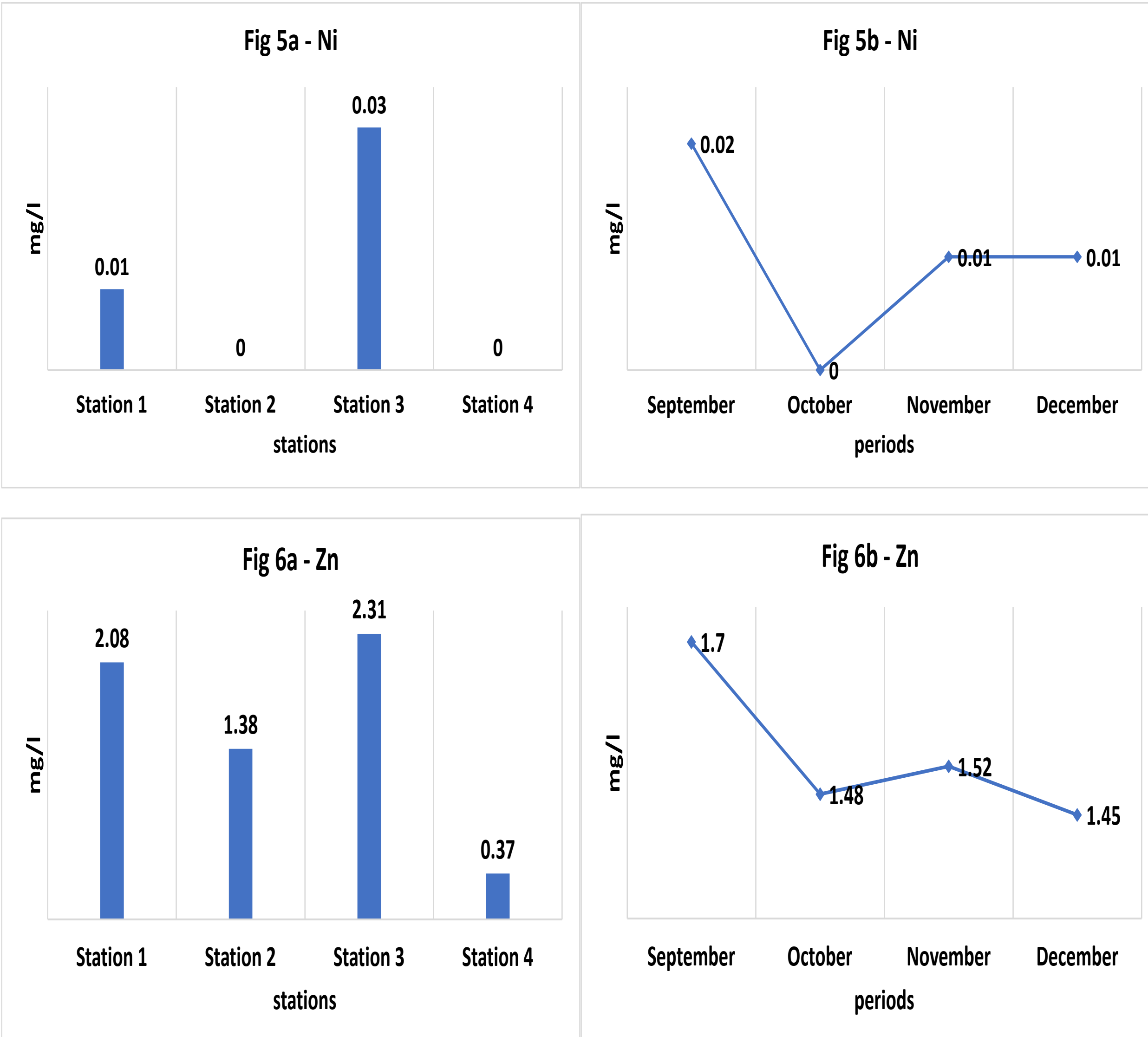
Figs. 2 – 4: Spatial and Temporal variations of heavy metal concentrations in the study area.



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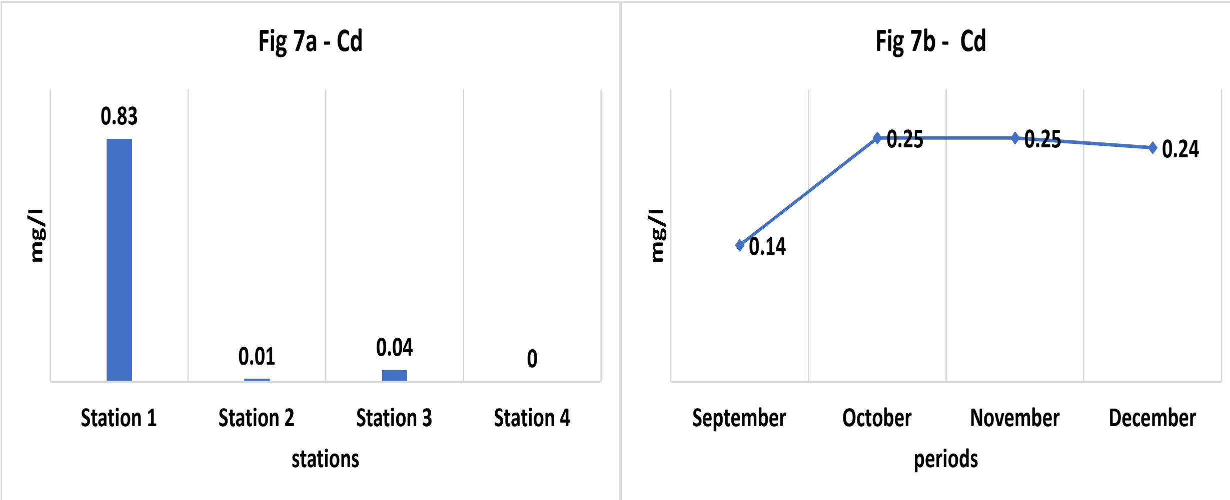

Fig 5 – 7. Spatial and Temporal variations of heavy metals in the study area (Contd).

The principal component analysis (Fig. 8) indicated that stations ST1 and ST2 could be in one cluster due to the concentration of Zn as a component 1 variable with Eigen values above 1 and 82.4% variance. Stations 3 and 4 could also be clustered together due to the concentration of Pb in these stations but these were on principal component 2 with less than 1 Eigen values and about 16% variance.

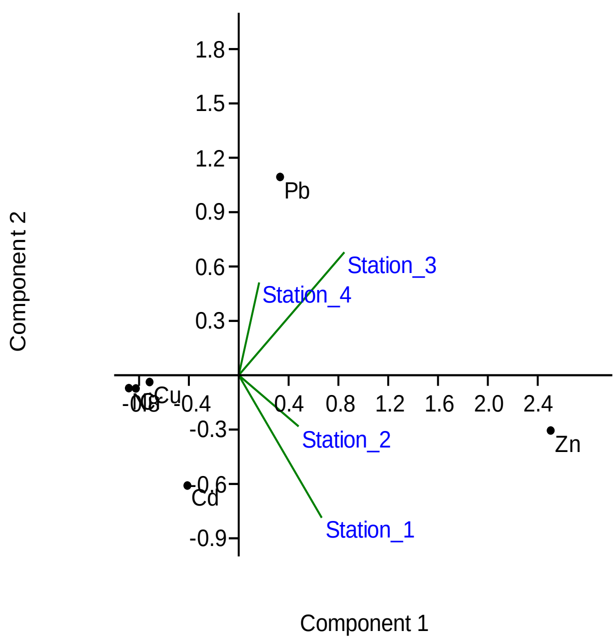

Fig. 8: PCA of heavy metals in the study area.

Discussion

Surface water pollution by heavy metals due to effect of over population and industrialization has become a major health risk concern. Treatment and management of wastes / effluents before discharge into the environment remains very key, however monitoring of the environment remains vital to the detection of levels of pollutants in the environment. Aquatic environment is one of the major receiving ends for pollutants, particularly heavy metals which are routed back into the food webs through bioaccumulation in aquatic macroinvertebrates, invertebrate fishes and finally biomagnified in humans (Edward et al 2013). The higher presence of heavy metals in aquatic systems also facilitate the production of reactive oxygen species that can damage physiological processes in fishes and other aquatic organisms (Akinnifesi et al. 2021). The mean concentrations of Pb (0.03±0.01 - 1.55±0.25 mg/l) was generally above the limits of the WHO while those of Cr (0.01±0.01 - 0.07±0.10 mg/l) observed in the current study were within the permissible limits (Cr – 0.05 mg/l) of the World Health Organization (WHO, 2004). This however, indicated increasing concentration of heavy metals in the study area particularly around the Iwofe axis with higher anthropogenic activities. The increase in the level of heavy metals concentration in Station 4 could also be attributed to the influx of various contaminants from the area into the river. These

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observations are similar to the reports of Ideriah et al. (2012) who reported five major sources of heavy metals viz: geological weathering, (natural phenomenon), the industrial processing of ore and metals, the disposal of metals and metal components, leaching of metals from garbage and solid waste heaps and animal / human excretions. Through various routes mentioned above are some of the entrance pathways for the high heavy concentrations observed in the study area, the concentration of companies around the Iwofe axis of Port Harcourt could be a contributing factor to the status of the heavy metal in the river investigated. The concentration of Pb observed in the current study was within the values (0.23 ± 0.00 mg/l) earlier reported by Moslen and Ekweozor (2017) in a creek within the Niger Delta. Pb is a potent toxin that could harm and impair biological tissues including the nervous system even at marginal concentrations. Public concerns with chromium are primarily related to hexavalent compounds owing to their toxic effects on humans, animals, plants, and microorganisms. Risks for human health range from skin irritation to DNA damages and cancer development, depending on dose, exposure level, and duration (Tumolo et al. 2020). Moslen and Aigberua (2018) earlier reported the concentration of Cr in surface water to be generally <0.001 mg/l but with mean maximum value of 0.09 ± 0.044 mg/l in the Niger Delta area. Copper is an essential element but high concentrations could be detrimental. It has been stated that eating or drinking too much copper could cause headaches, vomiting, diarrhea, stomach cramps, nausea, liver damage, and kidney disease (NIH, 2022). High levels of copper may damage red blood cells and may also reduce the ability of red blood cells to carry oxygen (MDH, 2023). The mean concentrations of Cu (0.00±0.00 - 0.09±0.03mg/l) was within and above the WHO limits of 0.02 mg/l. An elevated Cu concentration was also recorded around the Iwofe axis of the study area. The values of copper in the current study were within that (<0.001 - 0.02 ± 0.006 mg/l) observed by Moslen and Aigberua (2018) in the study area. The sources of nickel introduced into the environment can be from both natural and man-made origins. The concentrations of Ni (0.00±0.00 - 0.03±0.01 mg/l) was highest around the Iwofe axis and this was at variance with mean concentration of Ni (0.20 ± 0.01 mg/l) reported by Moslen and Ekweozor (2017). Moslen and Aigberua had also reported mean concentration of Ni in the range of <0.001 – 0.129 ± 0.006 mg/l. Elevated levels of zinc in drinking water may cause the water to have a milky, chalky, or turbid appearance and a metallic/astringent taste. The symptoms of zinc poisoning include "low blood pressure, urine retention, jaundice, seizures, joint pain, fever, coughing, and a metallic taste in the mouth" (McMahon, 2023).The mean range of Zn (0.37±0.13 - 2.31±0.15 mg/l) in the current study was below the 3.0mg/l limit of the WHO while those of Cd (0.00±0.00 - 0.83±0.26 mg/l) were within and above the 0.05 mg/l limits of the WHO. The highest concentration of Zn was observed around the Iwofe axis while that of Cd was recorded at the Choba axis of the study area. The values of zinc in the current study were generally above mean concentrations of Zn (0.23 ± 0.00 mg/l) earlier reported within the Niger Delta (Moslen and Ekweozor, 2017) but generally higher than values (<0.001 –0.132 ± 0.047 mg/l) reported by Moslen and Aigberua (2018). Cadmium is highly toxic to the kidney, and it accumulates in the proximal tubular cells in higher concentrations. Thus, cadmium exposure can cause renal dysfunction and kidney disease. Also, cadmium exposure can cause disturbances in calcium metabolism, formation of renal stones and hypercalciuria. Cadmium is also classified as group 1 carcinogen for humans by the International Agency for Research on Cancer (Obasi and Akudinobi, 2020). The concentration of Cd in the current study was generally above the limits of the WHO in all the stations except at station 4. Oribhabor and Ogbeibu (2009) had also reported the minimum and maximum concentrations of heavy metals in a creek of the Niger Delta in the range of 7.21-228.5 mg/l for Ca, 51.18-428.3 mg/l for Mg, 0.01-6.78 mg/l for Fe, 0.010-0.43 mg/l for Zn, 0.01-0.61 for Pb, 0.01-0.11 for Cd, 0.01-1.49 mg/l for Cr, 0.01-2.73 mg/l for Ni, while Hg was approximately 0.01 mg/l during the study period

Conclusion

The New Calabar River is one of the major rivers that supports biodiversity of living organisms and livelihoods. The study found gradual elevation of heavy metal concentrations particularly along the Iwofe axis of the river. This was attributed to the presence of anthropogenic activities within the area. Such activities generate both organic and inorganic wastes that eventually find their way to the aquatic water body. Bioaccumulation of heavy metals magnified along the food chain pose major concerns of health risk. It is therefore, important to monitor such aquatic environments in order to detect changes in the concentration of pollutants in the ecosystem.

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