International Journal of Fisheries and Aquatic Studies 2018; 6(2): 436-441

E-ISSN: 2347-5129
P-ISSN: 2394-0506
(ICV-Poland) Impact Value: 5.62
(GIF) Impact Factor: 0.549
IJFAS 2018; 6(2): 436-441

www.fisheriesjournal.com
Received: 21-01-2018
Accepted: 26-02-2018

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Assessment of heavy metal pollutants (Zn & Pb) in new calabar river, Niger delta, Nigeria

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Abstract
This study was conducted to determine the concentration of lead (Pb) and Zinc (Zn) in a fish species (*Sarotherodon melanotheron*), sediment and water from three different stations along Choba axis of New Calabar River, within the Niger Delta, Nigeria. Station one was located upstream of the river, very close to slaughter; Station two was located midstream and it is close to Indomie factory while station three was located downstream with no industrial activity. The samples were analyzed for Lead and Zinc content using Atomic absorption spectrophotometer (AAS VGB 210 system). The results were compared with the permissible limits given by World Health Organization (WHO) and Nigerian Federal Ministry of Environment (FMENV), which is given as 3.0 (mg/l) for Zinc and 0.01(mg/l) for Lead. The result for Lead in fish ranges from 1.49-8.06mg/l and Zinc in fish ranges from 7.3-29.25mg/l and the range for water is 0.001 (which was found below detection limit of the instrument). The result for Zinc in fish and Lead in fish were all above the permissible limits which is given as 3.0 (mg/l) for Zinc and 0.01(mg/l) for Lead. The results also showed that the New Calabar River is contaminated with heavy metal (Zinc and Lead). Hence the key recommendation is that strict compliance to regulatory standards on limits of effluents by anthropogenic activities and industries located along the stretch of the river should be enforced by the relevant regulatory bodies such as National Environmental Standard regulatory agency of Nigeria (NESREA), Federal Ministry of Environment (FMEMV) and Nigerian Oil Spill Response and Detection Agency (NOSDRA). Effort should also be made to ensure that Zinc and Lead and other heavy metals do not exceed the prescribed World Health Organization (WHO) and Federal Ministry of Environmental acceptable limits.

Keywords: heavy metals, fish, water, sediment, new calabar river and Niger delta

1. Introduction

The river is subjected to effluent discharge from industries sited along its banks. Among environmental pollutants; metals are of particular concern because of their potential toxic effect and ability to bio-accumulate in aquatic ecosystem [1]. The term pollution generally refers to alteration of the natural physico-chemical characteristics of an entity, medium or matter as a result of the presence of substances or compounds that are not supposed to be present in it or that are present in quantities and qualities that would limit the natural balance of the particular entity, medium or matter [2].

Fish living in polluted waters tends to accumulate heavy metals in the tissues. Generally accumulation of heavy metals by fish depends on several factors. These factors include metal concentration, duration of exposure, means of metal uptake, environmental conditions (water, temperature, pH, hardness and salinity) and intrinsic factors (fish age, feeding, and habitats).

The New Calabar River is among the important water resources in Niger delta region of southern Nigeria. The water serves as a source of livelihood for the artisanal fishermen in areas around Choba axis, as one of their important fishing grounds. There are several industries and maritime activities located within Choba axis of New Calabar River. Examples include waste discharges from industry, natural deposits. Any water contaminated with heavy metals is considered unsuitable as human portable water or for animal husbandry, irrigation, aquaculture purposes irrigation and even recreation. Humans are therefore in turn exposed to heavy metals by consuming contaminated plants, resulting in various biochemical disorders through the process known as bioaccumulation and biomagnification.

The Choba axis of the New Calabar River where this research is focused is a source of food fish for artisanal fishers and local consumers. The environment has a high concentration of anthropogenic activities such maritime companies, therefore the discharge of industries and domestic effluents is observed to be highly prevalent. Consequently, analyzing the heavy metals concentrations of selected media of the aquatic environment within the study area will show the extent to which the food source from the water particularly fisheries resources is contaminated. The results of the research is therefore expected to guide the evaluation of the how safe or otherwise fish food sourced from that area of New Calabar River is for human consumption.

2. Materials and Methods

2.1 Description of study area

The study was carried out along Choba axis of New Calabar River. The river, which is located in the coastal area of Niger Delta empties into the Atlantic Ocean (Figure 1). It is one of the important water resources in the Niger Delta in Southern Nigeria and is located along the outskirts of the crude oil city of Port Harcourt, in Rivers State. The river is located between latitude 4°25' N and longitude 7°1'60" E with the Delta itself having a bearing of 5°45'N and 6°35'N in latitude and 4°50'E and 5°15'E in longitude. Covering a land mass of some 70,000 Km^2, the Niger Delta accounts for about 8% of Nigerian land mass [3].

[4] described the New Calabr River as black in colour and tidal. The river contains fresh water at its upper and middle reaches but brackish towards the mouth. The University of Port Harcourt is located within the middle reaches of the river, The annual rainfall of the region is between 2,000mm and 3,000mm [5], while the dry season lasts from around March to October and occasional rainfall experienced even during the dry season months of about November to March.

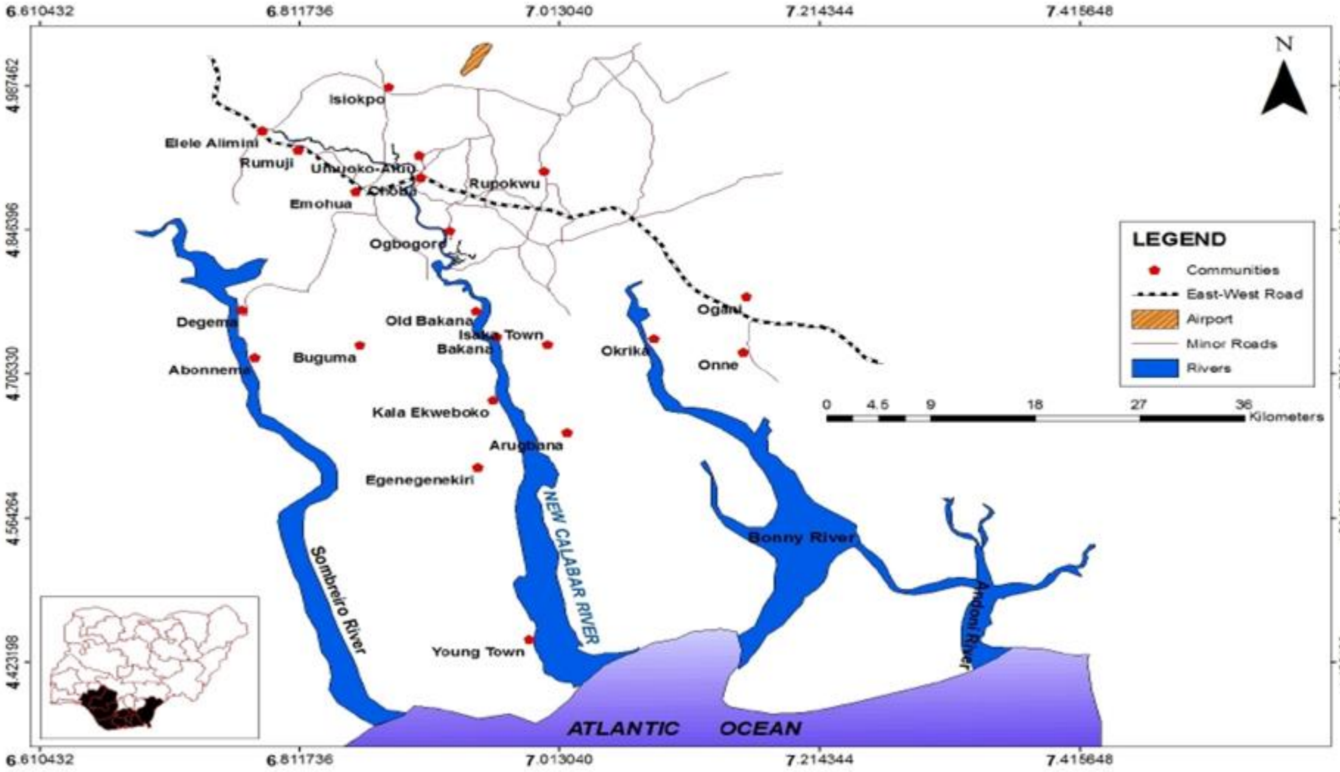

Fig 1: Map of lower Niger Delta showing the New Calabar River drainage system and study area. Inset is map of Nigeria showing position of the lower Niger Delta

2.2 Sampling Stations

The study was carried out along Choba axis of new Calabar River, close to Indomie industry and slaughter. Nigeria. Three different stations designated as upstream, midstream and downstream constituted the sampling stations for the different media of study. The basis for so classifying the stations is the determined direction of water flow in the river continuously from station one to the direction of station three and beyound. Station one was located upstream of the river, very close to an animal slaughter facility; Station two was located midstream and it is close to the Port Harcourt "Indomie" factory, while station three was located downstream which was devoid of any industrial activities throughout the duration of the study. Station 1 has coordinates of longitude E006 53 53.9" latitude N04 53 20.3", Station 2 has a coordinate of longitude E006 53 53.0"and latitude of N04 52 46.7", while Staition 3 is located downstream with a coordinate of longitude E006 54 03.5"and a latitude of N04 52 16.7".

2.3 Collections and Analysis of Samples

2.3.1 Fish samples analysis: they were collected from the water body using a cast net, while water samples were collected using plastic containers and sediments collected using the Eckman grab implement from the different stations. The fish sample collected was *Sarotherodon melanotheron.* This specie was chosen as it has been observed to constitute one of the most commonly occurring specie in the river and it is also often caught as food fish by artisanal fishers in the area. Therefore utilizing such a specie is considered justified as a major indicator how safe or otherwise food fish caught form the New Calabar River are [6].

2.3.2 Laboratory procedure for fish sample analysis

Fish samples: the obtained fish samples were immediately preserved in ice and transferred to the laboratory where they were refrigerated to preserve their freshness before analysis. Two grams (2g) of finely ground and oven-dry 60 ºC fish

material was weighed into a 30ml porcelain crucible. The sample was ignited in a muffle furnace for 6-8 hours or overnight at a temperature between 450 ºC and not exceeding 500 ºC.
Greyish white ashes were obtained indicating incomplete ignition. Another sample was weighed and the ignition was repeated. Samples were cooled on top of asbestos sheet and 5ml Nitric Acid (1N HNO3) solution. Samples were evaporated to dryness on a steam bath or a hot plate at low heat under ventilation. Samples were returned to the furnace and heated at 400ºC for 10-15 minutes until it was white or grayish white ashes were obtained. The sample was cooled on top of asbestos sheet 10ml Hydrochloric Acid (1N HCl) solution and was filtered into 20ml volumetric flask. The crucible and filter papers were washed with additional 10ml portion of 0.1N HCL solution. The filtrate was stored for K, Ca Mg, Na and P determination.

2.3.3 Laboratory procedure for water sample analysis (Digestion procedure APNA 1955): About 100cm^3 of a well-mixed water sample were measured into a 150cm^3 beaker. 5cm$_3$ of Nitric Acid (HNO_3) was added. Solution was evaporated to near-dryness on hot plate by making sure the sample didn't boil. Low medium heat was used. The beaker and the content were cooled to room temperature. Another 5cm^3 conc. Hydrocarbon (1N HC) was added to the beaker. The beaker was covered immediately with watch glass. The beaker was returned to the hot plate and a gente reflux action of the solution was set by increasing the temperature of the hot plate that is medium to high heat. The heating was continued with addition of concentrated Nitric Acid (HNO_3) until light-coloured residue was obtained i.e. digestion is completed. Additional 1-2cm^3 conc. Nitric Acid (HNO_3) was added to the residue and was washed with distilled water and was filtered into 100cm^3 volumetric flask and silicate and other insoluble materials were removed. Finally the solution was stored in 125cm^3 polypropylene bottle.

2.3.4 Heavy metal analysis: The heavy metals analyzed were Lead and zinc. These two parameters were chosen as they were suspected to have high concentrations in the studied media given the nature of industrial effluents continuously discharged into the water. The parameters were determined in samples of fish, sediment and water using computer controlled Atomic Absorption Spectrophotometer (AAS VGB 210 System). The instrument setting and operational conditions were done in accordance with the manufacturers' specifications.

2.3.5 Statistical Analysis
Data generated was analyzed using a two way analysis of variance (ANOVA) and Duncan's multiple range and results were tested for statistically significant differences at the 0.05.

3. Results
3.1 The mean Physico-Chemical Parameters of the New Calabar River in the Sampled Stations (February to July, 2017)
The highest mean dissolved oxygen values was recorded in station 2 (6.03mg/l) while the lowest was in station 1 (4.70 mg/l) in the increasing order: Station 2**<**Station 3**<**Station 1 and there was significant difference (p<0.05) across the mean values of the different station. Temperature was higher in station 2 (27.4 ^{0}C) while the lowest was observed in station 1 (26.7 ^{0}C). There was no significant difference (p>0.05) recorded among the three stations. The mean conductivity was highest in station 1 (130.7ms/cm) while the lowest was recorded in station 3 (61.17ms/cm). There was significant difference (p<0.05) across the different stations. Station 3 recorded the highest salinity value (18.1ppt) while the lowest was observed in station 3 (12.3ppt). There was significant difference (p<0.05) across the mean values from the three stations. The mean pH value was highest in station 2 (7.1) while the lowest was observed in station 3 (6.7). No significant difference (p>0.05) was observed between station 1 and station 3, but there was significant difference (p<0.05) between station 2 and the other stations. The mean value of the total dissolved solid was highest in station 1 (96.4mg/l) across the three stations (Table 1).

Table1: Results of Mean Physico-Chemical Parameters of the New Calabar River (Feb-July 2016).

Parameters	Station 1	Station 2	Station 3	Remark	DPR (2002)	FEPA (2003)
DO mg/l	4.70±0.07^c	6.03±0.33^a	5.37±0.33^b	S	20	-
Temperature (^{0}C)	26.7±0.33^a	27.4±0.29^a	27.18±0.31^a	NS	30	27.8/30
Conductivity (ms/cm)	130.7±0.49^a	65.0±0.45^b	61.17±0.31^c	S	-	<200-1000
Salinity	16.5±0.131^b	18.1±0.70^a	12.34±0.38^c	S	-	-
Ph	6.8±0.060^b	7.1±0.052^a	6.70±0.06^b	S	6-9	6.5-8.5
TDS	96.4±0.20^a	42.03±0.2^b	36.8±0.12^c	S	2000	1000/200

$^{a-c}$ *Means with similar superscript in the same row are not significantly different (P>0.05)*
NS: Not significantly different
S: significantly different

Table2: Mean concentration of Lead and Zinc in The different media (Feb-July 2016)

Different media	Biota		Sediment		Water		WHO(2011)	FEPA
	Max	Min	Max	Min	Max	Min	Approved limit	Approved limit
Zn (mg/l)	8.0	2.01	8.6	4.9	0.001	0.001	1.0	0.01
Pd (mg/l)	27.2	6.6	40.0	8.6	0.001	0.001	0.01	0.01

3.2 The mean values of Heavy metal (Zn and Pb) of the New Calabar River in the Sampled Stations (February to July, 2016)
The highest mean lead concentration in the fish sample *S. melanotheron* was in the month of January (8mg/l) while the lowest was in the month of April (2.01) in the increasing order: January<February<March<May<June<April. No significant difference (p>0.05) was observed across the month of February, March, April May and June. No significant difference (p>0.05) was observed between the month of

January and April but there was significant difference ($p<0.05$) between the mean lead concentration in January and the other months. The highest zinc concentration in the fish sample was observed in January (27.2mg.l) while the lowest was in the month of June (6.57mg/l). No significant difference ($p>0.05$) was observed between the month of January, February and March. A significant difference ($p<0.05$) was observed between the three month and April. Although no significant difference ($p>0.05$) was also observed between the month of June and July. The highest lead concentration in the sediment was in the month of March (4.85mg/l) while the lowest was in the month of February (0.00mg/l) in the increasing order: March<January<April <June<May<February. There was significant difference ($p<0.05$) across the six months. The highest mean zinc concentration in the sediment was recorded in the month of March (40.02mg/l) while the lowest was in the month of January (8.6mg/l) and a significant difference ($p<0.05$) was observed among the month six months. The concentration lead (0.001mg/l) and zinc (0.001mg/l) in the water very low across the six month but higher as compare to the WHO limit for heavy metal concentration in water (Figure 1).

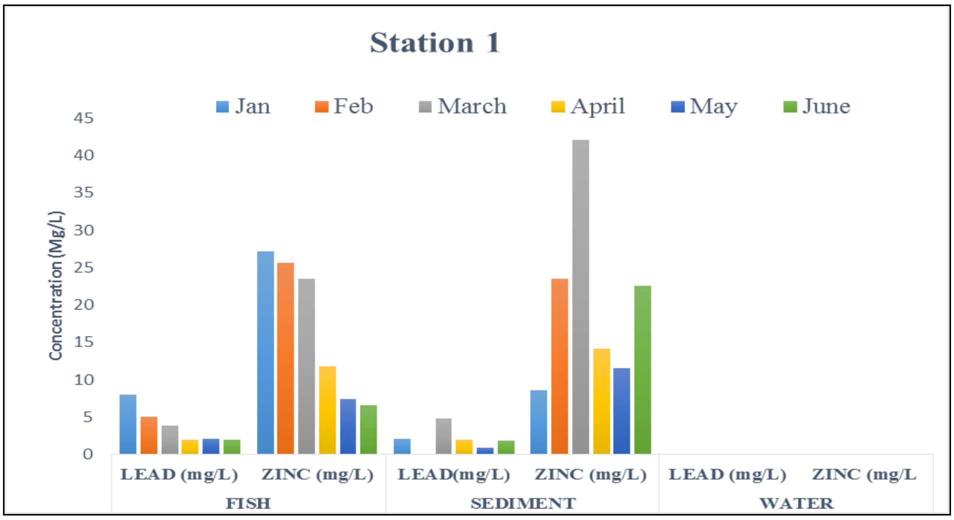

Fig 1: Mean concentration of heavy metals in station one

The highest mean lead concentration in the fish sample (*S. melanotheron*) was in the month of January (6.01mg/l) while the lowest was in the month of April (1.49mg/l) in the increasing order: January<June<March<February <May<April. No significant difference ($p>0.05$) was observed in the lead concentration across the six months.

The highest zinc concentration in the fish sample (*S. melanotheron*) was observed in January (29.3mg.l) while the lowest was in the month of April (9.85mg/l). No significant difference ($p>0.05$) was observed between the month of January, February, March and June. No significant difference ($p>0.05$) was also observed between April and May too. But April and May were significantly difference ($p<0.05$) from the other months.

The highest lead concentration in the sediment was observed in the month of March (1.67mg/l) while the lowest was in the month of April (0.98mg/l) in the increasing order: March<January<May<February<June<April. There was significant difference ($p<0.05$) across the six months. The highest zinc concentration in the sediment was recorded in the month of January (8.75mg/l) while the lowest was in the month of May (8.78mg/l) and there was a significant difference ($p<0.05$) among the month six months. The concentration lead (0.001mg/l) and zinc (0.001mg/l) in the water very low across the six month but still higher as compare to the WHO limit for heavy metal concentration in water (Figure 2).

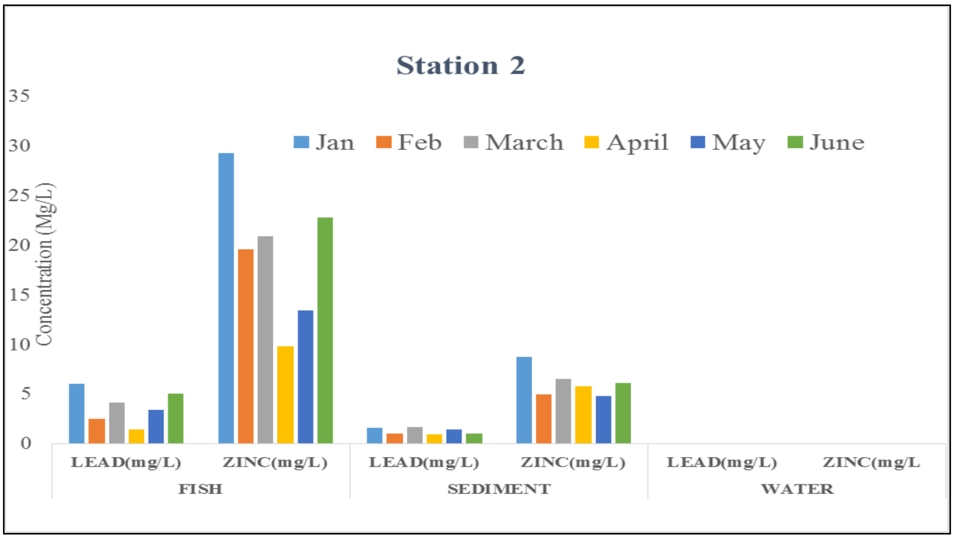

Fig 2: Mean concentration of heavy metals in station two

The highest mean lead concentration in the fish sample (*S. melanotheron*) was in the month of June (5.08mg/l) while the lowest was in the month of May (1.49mg/l) in the increasing order: June<January<February <April<March<May. No significant difference (p>0.05) was observed in the lead concentration across the first five months but the month of June was significantly difference (p<0.05) from others.
The highest zinc concentration in the fish sample was observed in May (24.4mg.l) while the lowest was in the month of March (16.85mg/l). No significant difference (p>0.05) was observed between the month of January and May.
The highest lead concentration in the sediment was observed in the month of April (1.87mg/l) while the lowest was in the month of May (0.77mg/l) in the increasing order: April<March<June<February<January<May. There was no significant difference (p>0.05) across the six months. The highest zinc concentration in the sediment was recorded in the month of March (9.5mg/l) while the lowest was in the month of May (2.99mg/l). No significant difference (p>0.05) was observed between January, February, March, April and June but there was a significant difference (p<0.05) between May and the other five months respectively. The concentration lead (0.001mg/l) and zinc (0.001mg/l) in the water very low across the six month but still higher as compare to the WHO limit for heavy metal concentration in water (Figure 3).

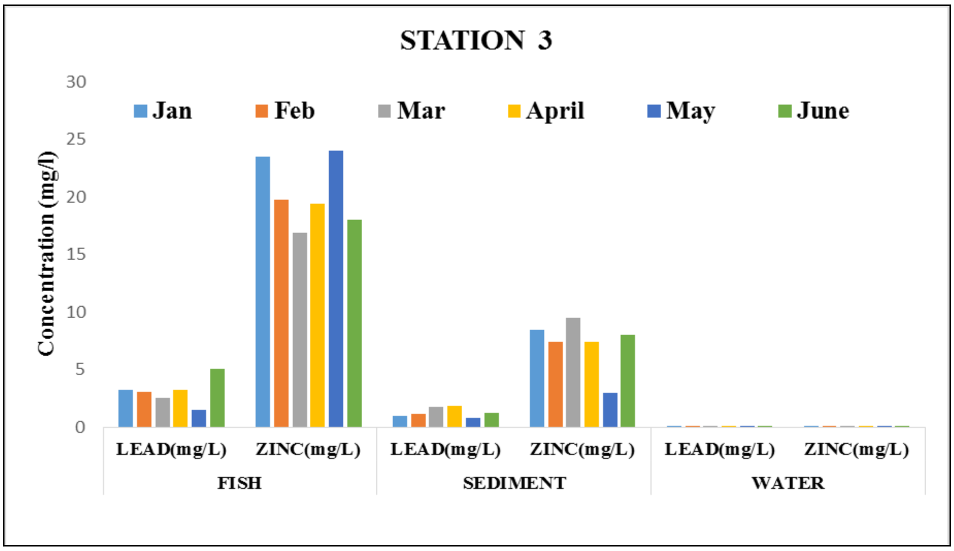

Fig 3: Mean concentration of heavy metals in station three

4. Discussion
Heavy metals have been reported by many researchers as major pollutants of environmental concern which constitute hazardous substances that are non-degradable and has the ability to cause serious danger to aquatic life and its environment [7, 8]. The results from the laboratory analysis of the different test media from the three stations showed that zinc consistently had the highest concentrations in the fish samples across the six months followed by the sediment. The trend of variation of the studied metals in the fish can be explained by the principles of bio-accumulation via absorption and adsorption [10]. This could also be attributed to the fact that the intestine is potentially the most important organ for zinc absorption [11]. Although some organic pollutants may metabolize and break down rapidly in the intestine, water soluble pollutants will be excreted, and other fat soluble pollutants dissolve in fatty tissue of the fish [12].The highest concentration of Zinc (Zn) was recorded in fish (29.3mg.l) as compared to the sediment and the water samples across the six months and this could also be attributed to the fact the fish *Sarotherodon melanotheron*. Is a benthic fish found at the bottom of the sediment where they take up more of the heavy metals as part of their food [13]. Other studies have shown that fish is able to accumulate more heavy metals like Cu, Zn, and Pb in the natural environment and should be used for biomonitoring [14].

The metal level of lead and zinc determined in fish, sediment and water are all above the acceptable limits recommended by regulatory bodies like the world health organization (WHO) which is an indication that this aquatic ecosystem of Choba axis of New Calabar river is significantly contaminated with these two heavy metals (Zn and Pb).

5. Conclusion
Heavy metals are diverse and conservative pollutants that bio-accumulates and bio-magnify along the food chain with deleterious effects on the aquatic ecosystems. The levels of lead and zinc observed in the different studied media (Fish, Water and Sediments) were above the acceptable limits as recommended by the World Health Organization (WHO). The water of New Calabar River, along Choba axis is highly contaminated with heavy metals. The consistent high values of Pb and Zn in the Fish as against sediment and water could be attributed to the different dynamics of the different media in the aquatic environment. In water, the dilution effects of the flowing river is suggested to be responsible for the recorded low levels of these metals in the water medium, when compared with the fish and sediment media samples studied [15]. Generally, the indicated presence of Pb and Zn in the studied environment is largely attributable to the presence of high anthropogenic activities around the stretch of the river studied, which is a source of discharge of heavy metal containing pollutants from industrial, domestic and agricultural and other human activities.

6. Recommendations
The following recommendations are made based on the findings of this study, as a means for reducing the impact of heavy metals in the New Calabar River:

1) Efforts should be made to ensure that zinc and lead and other heavy metals do not exceed the prescribe World Health Organization (WHO) and Federal Ministry of Environment (FMENV) acceptable limits.
2) To achieve a reduction of the level of these metals in sediments and fish; environmental policies and their implementation should be enhanced and targeted campaigns carried out to educate the public on the importance to protect and preserve aquatic systems and their resident biota by not discharging toxic containing wastes/effluents into the river.
3) Strict compliance to regulatory standards on limits of effluents by industries located along the stretch of the river should be enforced by the relevant regulatory bodies such as National Environmental Standards regulatory Agency of Nigeria (NESREA), such as Federal Ministry of Environment (FMENV) and Nigerian Oil Spill Response and Detection Agency (NOSDRA).
4) Constant Environmental monitoring programmes and researches of this nature should be conducted routinely to evaluate the status of different heavy metals in the environment.

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