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Bioaccumulation of Selected Heavy Metals (Cd, Zn, Pb and Cr) in the Tissue of Mudskipper (*Periophthalmus papilio*) from Lelasibokpo Creek, Bodo City, Gokana L.G.A, Rivers State, Nigeria

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Abstract

The activities and progress of industries have led to increased emission of pollutants into ecosystems. The Lelasibokpo Creek is one of the most important aquatic ecosystems in Bodo City, Gokana LGA, Rivers State, Nigeria. It has received effluent discharges and crude oil pollution from heavily industrialized and highly populated settlements. So, studies to ascertain the levels of heavy metals in this marine environment and determine potentially hazardous levels for man are necessary. In this investigation, concentration of heavy metals Cd, Zn, Pb and Cr in mudskippers were determined using appropriate laboratory procedure. Heavy metal concentration in Lelasibokpo creek decreased in the order of Zn>Cr>Pb>Cd. The highest concentration of heavy metal observed in Zinc was 15.6656 ±4.5mg/kg and the lowest in Cadmium 0.8044 ±0.8mg/kg. The physiochemical parameters of pH, BOD, COD, Turbidity, Salinity, DO, TDS and Conductivity were also determined and varied within the three stations in their concentrations. The heavy metal concentration was not statistically significant and their concentrations exceeded the permissible limits for heavy metals as stipulated by WHO and FEPA (now the Federal Ministry of Environment). This calls for serious concern thus, a serious notification to industrial and manmade pollution, which can lead to marine habitat and food chain contamination, is necessary and important.

Keywords: Lelasibokpo Creek, Mudskipper, Heavy Metal, Physiochemical parameters

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INTRODUCTION

Environmental pollution and its hazards are the most important problems of societies and living creatures. On the other hand, increased population with the development of technology and production can cause a lack of attention to environmental safety (Saravi *et al.*, 2009). Industrialization leads to the pollution of ecosystems. Therefore, recognition of pollutants and prevention of their environmental dispersion are some of the requirements in this field. It is important to determine the sources of pollution, their marine environmental effects and methods of containment.

Filtration of industrial wastewater and public enlightenment campaigns on environmental protection are essential in the control of pollutant pollution.

Heavy metals represent a group of the most important pollutants which cause environmental degradation in coastal areas. Heavy metals are introduced into the aquatic ecosystems in a number of ways. These chemicals accumulate in the tissues of aquatic organisms at concentrations many times higher than concentrations in water and may be biomagnified in the food chain to levels that cause physiological impairment at higher trophic levels and in human consumers (Raposo *et al.*, 2009).

Heavy metals are natural constituents of the Earth's crust and are present in varying concentrations in all ecosystems. During the past two decades, high levels of heavy metals and their compounds, both inorganic and organic, have been released into the environment as a result of a variety of anthropogenic activities (Komarnicki, 2005). From an environmental point of view, coastal zones can be considered as the geographic space of interaction between terrestrial and marine ecosystems that is of great importance for the survival of a large variety of marine species, including plants and animals (Castro *et al.*, 1999). Coastal pollution has been increasing significantly over the recent years and found expanding environmental problems in many developing countries.

Urban and industrial activities in coastal areas introduce significant amounts of heavy metals into the marine environment, causing permanent disturbances in marine ecosystems. These lead to environmental and ecological degradation and constitute a potential risk to a number of flora and fauna species, including humans, through food chains (Boran et al., 2010). Heavy metals were chosen as suitable pollutants because they are widespread environmental contaminants, from either natural or anthropogenic sources, and are widely believed to be a threat to the health and survival of many marine or aquatic animals, including crustaceans and fin fishes (Lorenzon et al., 2001). Accumulation of heavy metals in tissues mainly depends upon concentration of metals in water and exposure period; although some other environmental factors such as salinity, pH, hardness and temperature play significant roles in metal accumulation (Blackmore et al., 2003). The contaminated fish from aquatic environment may become a public health concern. Hence, it is important to determine the concentrations of heavy metals in commercial fish and shrimps in order to evaluate the possible risk of human consumption (Cid et al., 2001).

MATERIALS AND METHODS

Study Area: The study was conducted in the Lelasibokpo Creek, Bodo city. Bodo lies on the coastal lowland of the Niger Delta, and in the southern part of

Gokana Local Government Area of Rivers State. The community is about fifty-six kilometers by road from Port Harcourt and is located between latitude 4° 36'N and longitude 7° 21'E of the equator. Bodo is bounded on the north by communities of Gokana, on the East by the Andoni people, on the West by Okirika Kingdom and on the South by the Ibani (Bonny) and the Atlantic Ocean. There main occupation is fishing and farming and the community is surrounded with numerous rivers and seas of which Lelasibokpo Creek from which the sample was taken is one of them. Currently, serious anthropogenic activities are going on in the creek due to the on-going Ogoni clean-up by Shell Company of Nigeria.

Sample collection: The mudskipper samples were collected randomly from three different stations of Lelasibokpo Creek for analysis with hand and fishing net and were then transported immediately to the laboratory for experiment in an ice chest to avoid decay. Mudskippers taken from each station were place in a labeled container for proper identification and accuracy.

Water samples were also taken respectively from three different stations of the creek for physiochemical parameters analysis with labeled bottles for easy identification and accuracy. The bottles were buried about 10cm deep in the water and were brought out with the bottles filled with the water and then taken to the laboratory for analysis.

Procedure for the determination of heavy metals in the biota (Fish): The fish samples were randomly selected before they were crushed with mortar and pestle after they have been sliced into pieces with stainless knife. After the thorough crushing, 2-5g of these parts were weighed into the digestive vessels. The specimen samples were mixed with concentration aqua-regia acid of Nitric Acid NHO₃ and Perchloric Acid in the ratio of 3:1. About 20ml of distilled water was added. The beaker was later transferred to the hot plate where the digestion process was continued until a clear solution was observed with clear pale yellow colour or the initial volume of the solution reduced to one-third of its original volume. At this point, the digested sample was removed from the heating mantle

and allowed to cool before filtration into the measuring cylinder. The digesting vessels were rinsed with the distilled water and later poured into the filtrate through the filtrate funnel. This filtration solution was made up to 50ml mark with distilled water. This final filtrate was aspirated with the AAS instrument for the determination of metals of interest after the proper calibration of the equipment at appropriate absorbance wave length and the necessary standards that were prepared at different concentration such as 2ppm, 4ppm, 6ppm. etc.

The concentration of the metal of interest in the aspired samples was displayed on the screen and printed out as concentration of heavy metals in the analyzed samples.

Analysis of water chemistry (physiochemical parameters): pH (Hydrogen Ion Concentration) ASTM: The sample was measured using pH meter (pH meter, Jenway model No. 2010). Little quantity of the sample was put in a container or beaker and shaken thoroughly. The pH electrode was then immersed in a sample and the result read off from the meter and recorded. Prior to the pH measurement, a buffer solution was used to standardize the pH meter.

Dissolved Oxygen (DO): On the fifth day after sample collection and fixing, concentrated H₂SO₄ was added to the sample (and mixed thoroughly) giving it a pale yellow colour at complete dissolution. 50ml of the sample was then transferred into a 100ml Erlenmeyer flask, and two drops of prepared potato starch solution (as indictor) was added to the sample in the flask which then turned blue-black. This was then titrated against 0.025N Sodium Thiosulphate solution, until a colourless solution was formed. The final volume of Thiosulphate indicates the amount of oxygen present in the sample, and the result was expressed in mg/l.

Biochemical Oxygen Demand (APHA 5210): 250ml volume of the sample was treated with dilution water containing nutrients to the one litre mark and the initial DO record. 200ml of the diluted samples was incubated for 5 days at 20°C. The final DO

measurement was taken after the incubation. The BOD value was then obtained by subtracting the final DO from the initial DO and further dividing by the dilution decimal fraction.

Chemical Oxygen Demand (ASTM D1.252): COD was determined by adding 5ml N.8 potassium dichloromate and 10ml sulphuric acid into 100ml sample in the flask and mixed well. The sample was cooled in a tray containing cold running water. 1ml silver sulphate followed by 5ml of sample was added to the flask. This was mixed well and fixed up the condenser. The content was mixed and few anti bumping granules were added and refluxed for two hours. The sample was cooled, 45ml of water was added and placed under the cooled running tap until it's quite cold. One drop of ferrous 1:10 phenanthroline indicator was added and the residual dichromate was titrated with N/8 ferrous.

Total Dissolved Solid (APHA 25OC): TDS was measured by filtering 100ml of the effluent sample through grade 42c glass fiber paper by means of vacuum pump into a pre-weighed 100ml. This was gently evaporated, and then heated on a hot plate (Hotplate fisher Thermix model Nn218) to dryness and then heated to constant weight. The TDS was then calculated from the difference in weight.

Salinity: Horiba water checker (model 10) was used for the analysis of salinity. About 200ml of sample was put into the sample container. The mode was used to select the parameter (salinity) required and the value was read off from the screen of the instrument and recorded.

Turbidity: This sample was measured using nephelometry. The application range is 0-40 nephelometric turbidity unit (NTU).

Conductivity: This was measured with a probe and a meter. Voltage was applied between two electrodes in a probe immersed in the sample water. The drop of voltage caused by the resistance of the water was used to calculate the conductivity per centimeter. This was measured in the lab and it is usually measured in micro or millisiemens per centimeter (uS/cm or mS/cm).

Statistical Analysis

Data collected from the experiment were subjected to one-way analysis of variance (ANOVA), and student's t-test was used to assess whether samples varied significantly. Possibilities less than 0.05 (p<0.05) were considered as statistically significant.

RESULTS

The heavy metals had concentrations that exceeded the permissible limit for heavy metals as stipulated by

WHO (2008) and FEPA (2003). Though there were variations among stations (Table 1), they were not statistically significant. The heavy metals were in the order Zn>Cr>Pb>Cd. Results of the concentrations of the physicochemical parameters within the three stations in the three months of experimental execution are presented in Table 2. From the table, the physiochemical parameters varied in their concentrations within the three stations in three months of experimental execution and also in their permissible limit according to WHO and FEPA.

Table 1: Statistical Analysis of Results of Heavy Metal Concentrations in Lelasibokpo Creek, Bodo, Rivers State, Nigeria

Station	Cadmium	Lead	Zinc	Chromium	
	mg/kg	mg/kg	mg/kg	mg/kg	
Station 1	0.8411 ^a	3.5830 ^a	16.9960 ^a	11.5844ª	
	±0.8314	±2.0950	±5.0168	±4.9352	
Station 2	0.8044 ^a	3.5830^{a}	15.8420 ^a	10.8847 ^a	
	±0.8069	±2.1193	±4.1591	±5.4883	
Station 3	0.8707 ^a	4.1501 ^a	15.6656 ^a	10.5179 ^a	
	±0.8359	±2.1251	±4.4893	±7.3877	
P Value	0.995	0.931	0.929	0.976	
WHO/FEPA Permissible Limit	0.005/0.02	0.05	5.0	0.1	

The mean concentrations of the heavy metals are presented in Figures 1-4.

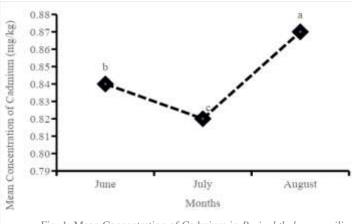


Fig. 1: Mean Concentration of Cadmium in Periophthalmus papilio from Lelasibokpo Creek, Bodo City, Gokana, Rivers State

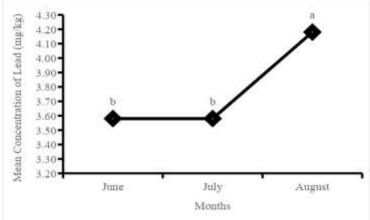
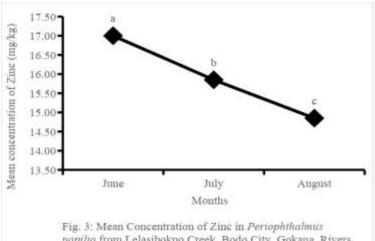


Fig. 2: Mean Concentration of Lead in Periophthalmus papilio from Lelasibokpo Creek, Bodo City, Gokana, Rivers State



papilio from Lelasibokpo Creek, Bodo City, Gokana, Rivers State

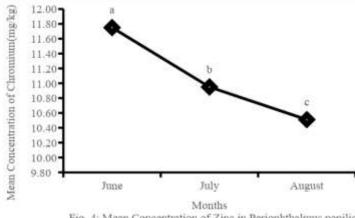


Fig. 4: Mean Concentration of Zinc in Periophthalmus papilio from Lelasibokpo Creek, Bodo City, Gokoana, Rivers State

Table 2: Statistical result of the three month's experiment of physiochemical parameters

Stations	рН	DO	BOD	COD	Salinity	Turbidity	TDS ^{×10-4}	Conductivit y (×10 ⁻³ (uS/cm or mS/cm).
Station1	6.834 ^a ±	31.333 ^a ±	34.00 ^a	41.000° ±	0.100^{a} ±	5.800 ^a ±	53.487 ^a ±	89.700 ^a ±
	0.306	1.185	±2.000	1.000	0.053	0.100	41.0208	87.109
Station2	$7.233^a ~\pm$	25.400 ^b ±	32.00°±	45.667a±	$0.050^{a}\pm$	$6.200^{ab} \pm$	53.167 ^b ±	87.000 ^b ±
	0.252	0.954	2.646	2.887	0.026	0.100	50.3322	16.703
Station3	$6.923^a~\pm$	26.600bc	26.63a	44.000a±	$0.047^a~\pm$	6.900° ±	65.333 ^{bc} ±	114.667 ^{bc} ±
	0.643	±1.819	±12.423	6.245	0.006	0.436	35.119	13.614
P-value	0.302	0.004	0.469	0.409	0.184	0.06	0.000	0.000

DISCUSSION

In this investigation, the value of cadmium (0.8411 ±0.8314). This may have been link to pollutants coming from crude oil exploration, agricultural and industrial processes. The result is considered higher than that reported in periwinkle (Tympanotonus fuscatus) samples from Uta ewa creek, Imo River estuary by Nsikak & Idopise (2020). Also found higher than that of Opeyemi et al (2018) found in tilapia fish. Although cadmium in this result has a high P-value of 0.995 which implies that it is above the maximum permissible limit range of WHO (2008) and FEPA (2003). A high level of Cd in the environment is hazardous, toxic and could negatively damage the kidney and other organs of human when consumed (Satarng 1984). etal., In the result from table above the mean value of lead

to the (8.96 - 20.35 mg/kg) observed in the various organs of *Clarias gariepinus* from the Ogun River (Farombi *et al.*, 2007). This variation and high increase may be adduced to the kind of anthropogenic activity that is going in the study

 (3.5830 ± 2.0950) is low compared to that observed by Opeyemi et al. (2018) in three aquatic fishes; tilapia fish, lobster and crab, with mean concentration of \pm 2.1, 31 \pm 1.1, 23 ± 1.3 , and 28 ± 1.4 mg/kg, respectively. Nsikak and Idopise (2020) also reported low concentration of lead. Nevertheless, lead was not detected in the research of Olowu et al. (2008). In this result, lead is within the permissible range approved by WHO (2008), SON (2002). Concentration of zinc ranges from 16.9960-5.0168 mg/kg, this is lower than the $(21.01\pm2.38 - 49\pm4.33 \text{mg/kg})$ recorded by Ahmed et al (2003) and (84.76 – 136.9) mg/kg gotten from Oreochromis niloticus in the Koycegiz Lake by Yilmaz (2009). But higher than $(12.70\pm0.54\text{mg/kg})$ reported by Owoh & Wokoma (2022) in the tissues of Tilapia Guineensis from Andoni River. (0.043±0.026 -0.031±0.005) values reported by (Abdullah et al., 2007) other reports from the Niger Delta Ekeanyanwu et al (2010) and Edem et al, (2009). It is however closely related areas.

The concentration of chromium varies within the range of $(11.5844^a \pm 4.9352 \text{ and } 10.5179^a \pm 7.3877)$ and it is therefore higher than the value of 3.26 ± 0.06 mg/kg reported

by Owoh & Wokoma (2022) in the tissues of *Tilapia Guineensis* from Andoni River, higher than the result obtained by Olowu *et al.* (2010)., and Nsikak & Idopise (2021)., The result of chromium in this study is lower comparatively to the values (20.89mg/kg) recorded by (Obot *et al.*, 2016). Adata *et al.* (2015) reported lower value compared to the value of the present study. pH varies within the three stations having station two as its highest concentration and station one the least the three stations are not statistically significant at p-value 0.05 although its p-value from the result is 0.302 indicating that it is slightly below the permissible limit stipulation by WHO (2007), SON (2002) and FEPA (2003).

Station one, has the highest level of dissolved oxygen while station two has the least. The three stations are statistically significant at p-value 0.05 and it is far below of permissible limit. Therefore, DO in that creek needs serious attention. From the table, station one has the highest Biochemical Oxygen Demand while station three the least but they are not statistically significant at p value. However, its p value is within the permissible range as approved by FEPA and WHO and so, concentration of BOD in the area of study is relatively normal.

The level of Chemical Oxygen Demand varies within the stations having station two as the highest while station one the least. It is not statistically significant at p value but it is below the permissible range. High level of salinity is seen at station one and the least at station three. The three stations are not statistically significant. Turbidity in Station

three has the highest level of turbidity while station one the least. The mean values are statistically significant at p value and it is below the permissible limit.

Total Dissolve Solids in Station three has the highest total dissolve solids while station two the least. The concentration is statistically significant. Conductivity in Station three has the highest level of conductivity while station two has the least. They are statistically significant at p-value and are below the permissible limit as stipulated by WHO and FEPA.

CONCLUSION

This study provides a baseline data related to heavy metal pollution stress in the Lelasibokpo creek in Bodo City, Gokana LGA and could help in designing strategies aimed at the management of the control of the metal pollution and associated with health risk. It is studied and observed that mudskippers gotten from lelasibokpo Creek in Bodo City is highly concentration with Heavy metal especially zinc which thus implies that the creek is heavily polluted, and are all above the permissible limit stipulated by WHO and FEPA. This may be as a result of human activities either from industries or individuals. Thus, federal government should intensify the ongoing Ogoni clean up and make sure that it been carried out by professionals and with the adequate equipment. The level of anthropogenic activities should be reduced and effluent discharge should be monitored.

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