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CONCENTRATIONS OF SOME HEAVY METALS IN TILAPIA (*SAROTHERODON MELANOTHERON)* FROM EKEREKANA CREEK IN THE UPPER BONNY ESTUARY

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Abstract
Heavy metals are naturally occurring elements but are also released into the environment from industrial processes, mining and other anthropogenic activities to levels that constitute pollution. High levels of heavy metals in aquatic organisms may pose a health risk to those consuming those organisms. The aim of this study was to evaluate the status of contamination of the Ekerekana creek in the Upper Bonny Estuary. Tilapia (*Sarotherodon melanotheron*)were collected from four different stations; the Point of discharge of refinery effluents into the Ekerekana creek (S1), the Boundary between Ekerekana and Okari creek (S2), refinery jetty (S3) and Ogoloma creek (presumed Control) (S4). The levels of Mn, Ni, Co, and Cr were determined using an Atomic Absorption Spectrophotometer (AAS). The mean concentrations of Mn, Ni and Co in the fish muscles ranged from 1.18 to 5.06mg/kg, 2.43 to 15.15mg/kg and 2.00 to 9.03mg/kg, respectively. The burdens of nickel and chromium were below the DPR target values. The concentrations of nickel in the fish muscles were found to be within the permissible limits of the United States Food and Drugs Administration; Cr was below detectable limits (<0.05 mg/kg) in the fish muscles. The metals studied were not found to be at levels above regulatory limits, but caution should be taken in consuming fish because of the possibility of an increase over time, especially when the refinery comes back into operation. It is recommended that further studies/continuous monitoring of heavy metals should be carried out especially when the operations of the refinery come back on steam.

Keywords: Concentrations, heavy metals, Tilapia, creek, bonny, estuary

Introduction
Fishes occupy a particular range in aquatic contamination studies because they have a vital role to play in the establishment of water quality guidelines and are also said to be a part of our diet (Burger & Gochfeld, 2005). The level of heavy metals in estuaries found in the Niger Delta in the past has been on the increase in recent times as a result of domestic wastes, wastes from industries, and agricultural waste (Kaoud, 2015). Then when these wastes are sent into the marine environment, they tend to cause great ecological changes, because of how toxic they are; their long-lasting existence, and their ability to accumulate in the organisms that inhabit the marine ecosystem. The refinery effluents are seen to be detrimental to public health, when components of petroleum such as aliphatic hydrocarbons as well as heavy metals drain into the river body (Ogbuagu et al., 2011; Okoli et al., 2011).

Fishes which are widely distributed aquatic organisms are found to be one of the main protein sources for humans. They are seen to be excellent heavy metal contamination indicators in the aquatic system since they occupy different levels of the food chain (Karadede-Akin & Unlu, 2007). The food chain and water are possible channels through which heavy metals get accumulated in the fish. These heavy metals may enter the bodies of fishes through their digestive tract, gills or body surface (Wang, 2015). Effectively, after absorption, the metal in the fish are been transported through the bloodstream to the organs and tissues where they get accumulated (Fazio et al., 2014). Any metallic chemical element with a relatively high density and toxicity at low concentrations is referred to as heavy metal. Examples include Hg, Cd, As, Cr, and Pb. Some heavy metals as trace elements (E.g Cu, Fe, Zn) are useful to maintain the human body's metabolism (Igwemmar et al., 2013). However, they can lead to poisoning at high concentrations. 'Heavy metals are members of a loosely defined subset of elements exhibiting metallic properties like water solubility, and strong attachment of polypeptides and proteins. Heavy metals occur naturally in the ecosystem having large varying concentrations. Most metals in the rivers and streams come in from industries, and municipal and urban run-off, causing harm to life (Tolcin, 2011).

The different levels of heavy metals concentrations found in fish tissues show the exposure level in the past, either through water and/or food which can show to a large extent the existing state of the animals before toxicity as it affects the interrelationship of the populations within the aquatic environment (Birungi et al., 2007). When these fishes that are contaminated with heavy metals are eaten, it could be injurious to the health of humans as these metals tend to accumulate in the tissues of the body to a hazardously poisonous level (Tchounwou et al., 2012; Jaishankar et al., 2014). Cu, Co, Cr, Ni, Zn and Mn as essential metals are needed in trace amounts (smaller than 0.01% of the organism's mass) in the diet and their absence may cause serious problems (Ekweozor et al., 2017). Non-essential metals like "Cd, Pb, As and Hg have no biological functions and could be toxic even in very small amounts".

Fishes are abundant in most bodies of water and can be found in nearly all aquatic environments. The metal concentrations vary with species relating to their feeding habits and bioaccumulation capacity (Akoto et al., 2014). The aquatic environment's contamination, uptake, regulation, and elimination inside the fish all have a direct impact on the heavy metal concentrations in the fish's numerous tissues and organs. (Effiong et al., 2019). Heavy metals when at a high level is said to have an evident lethal and chronic effects on fishes (Akan et al., 2012; Jaishankar et al., 2014). Hence, the use of fishes for evaluating the environmental situations in the aquatic environment has gathered grounds in recent times (Akan et al.,2012). The nutritional level and therapeutic effects of fishes has recently led to its consumption being on the increase. Fish contains a lot of protein and also some vital vitamins, unsaturated fatty acids and minerals (Medeiros et al., 2012). Fishes being at the top of the aquatic food chain, have a piled-up level of heavy metals uptake from food, water and even sediments (Abdulali et al.,2012). Fishes are one of the most abundant organisms found in nearly all aquatic environments. It's been estimated by The Food and Agriculture Organisation (FAO) that "about 1 billion people worldwide rely solely on fish as their primary source of animal protein". The metal concentrations vary with species relating to their feeding habits and bioaccumulation capacity (Akoto et al., 2014). *Sarotherodon melanotheron* (Rupell, 1852) also referred to as the black chin tilapia is of the class: Actinopterygii, Order: Perciformes, and Family: Cichlidae. It has a pale color and has a dark pigmentation seen on the chin. Adult *Sarotherodon melanotheron* can have a standard length of 28.0cm. (Bawa-Allah, 2007). *Sarotherodon melanotheron* are among the top aquatic organisms exposed to a high amount of heavy metals due to their feeding habits. They can filter out microscopic algae, invertebrates, and detritus from sediments (Ofori-Danson & Grace, 2016).

The activities of industries, mining, and domestic and agricultural activities have led to an increase in the rate at which heavy metals are discharged into the estuaries of the Niger Delta over the past decade (Kaoud, 2015). Research on the impacts of heavy metal pollution has been conducted in many ways as result of heavy metal pollution of the aquatic environment. Aquatic bodies can be polluted by agricultural runoff, industrial waste, and geochemical structures, which can have an impact on both the water quality and the aquatic animals that live there. The aquatic environment is one of the receiving ends for pollutants, heavy metals in particular which are moved back into the food chains when bioaccumulated in plankton and invertebrates to fishes and finally get biomagnified in man (Edward et al., 2013). Bonny River receives the effluent/wastewater that comes from the Port Harcourt Refining Company (PHRC) which is directly discharged into Ekerekana creek associated with the River and flows into other creeks and down the Bonny River. As in most parts of the Niger Delta, the oil exploration and exploitation in this region has to a large extent caused the environment to degenerate. The oil industry alongside many other industrial and economic activities and increased population has led to increased production of wastes, which are discharged carelessly. Wastes discharged directly or indirectly from domestic activities, refineries, and land-derived sources, impact the water quality of Bonny River and its environs. There are significant amounts of trace toxic metals in many municipal and industrial wastes. (Yusuf et al., 2003).

Studies carried out by Anaero-Nweke et al. (2018) on various concentrations of heavy metal in fish from the Upper Bonny Estuary showed "Cr and Ni to be above the FAO/WHO (2012) permissible limits of 0.5mg/kg and 0.6mg/kg respectively in fish muscles, but the values in the fish were compared to WHO limits for water by the authors". Muscles being an edible part of the fish pose a health concern. Javed and Usmani (2014) carried out research and it was found that "Chromium ranged from 9.72 to 200.48mg/kg in the different organs and tissues, Mn was 103.21mg/kg in gills and 9.24mg/kg in muscles, Ni was 17.49mg/kg in gills and 8.31mg/kg in muscles, Co was 3.87mg/kg in the muscles and 13.68mg/kg in the gills of the fish; *Channa punctatus* in the Rivulet water and it showed that Ni, Mn and Cr exceeded the limits, thereby making the water unfit". Umunnakwe and Aharanwa (2014) conducted an investigation in different fish species and found out that "Ni and Cd exceeded the permissible and the accumulation trend, read thus; Fe>Cd>Ni>Hg>Cr". The findings of Owhonda et al.(2016) showed that Nickel had a high concentration in the muscles of *Sarotherodon melanotheron* fish species. A major problem has been in the quality of water in the past century, and to meet acceptable standards, all effluents need to be treated before being discharged into the water body (John & Chimka, 2017). Hence the need for this study to see the extent to which these untreated effluents could impact the aquatic environment.

Aim and Objectives of the study

The main aim of this study was to evaluate the status of heavy metal (manganese, nickel, cobalt and chromium) contamination of the Ekerekana creek in the Upper Bonny Estuary which receives petroleum refinery effluents. Specifically, the objectives were to:

1. determine the concentrations of chromium, cobalt, manganese and nickel in fish muscle
2. evaluate spatial and temporal differences in the concentrations of the metals in fish muscles.

Materials and Methods

Study Area

The sampling stations were established in a creek of the Upper Bonny Estuary and Okrika River, Rivers State, Niger Delta. The estuary is an inter-tidal mangrove swamp. A major industrial outfit; the Port Harcourt Refinery Company (PHRC); a point source of discharge of industrial effluents generates several volumes of effluents channelled into the water body via a drainage system into the Ekerekana creek (Anaero-Nweke et al., 2018).

The sampled stations are:

- Station 1 – Point of discharge of refinery effluent into the Ekerekana Creek This station is located at N 04^0 44' 53.4" and E007^0 06' 05.7"
- Station 2 - Boundary between Ekerekana and Okari creeks. This station is located at N 04^0 44' 43.6" and E007^0 06' 05.5"
- Station 3 - Refinery jetty where the pipelines are situated and petroleum products are loaded. This station is located at N 04^0 44' 18.1" and E007^0 05' 55.4"
- Station 4 - Upstream of the refinery jetty (control station). This station is located at N 04^0 44' 53.4" and E007^0 06' 05.7"

All sampling points were geolocated with GPS and plotted on a map (Fig 1).

Sampling was done monthly in the months of September, October, December and January.

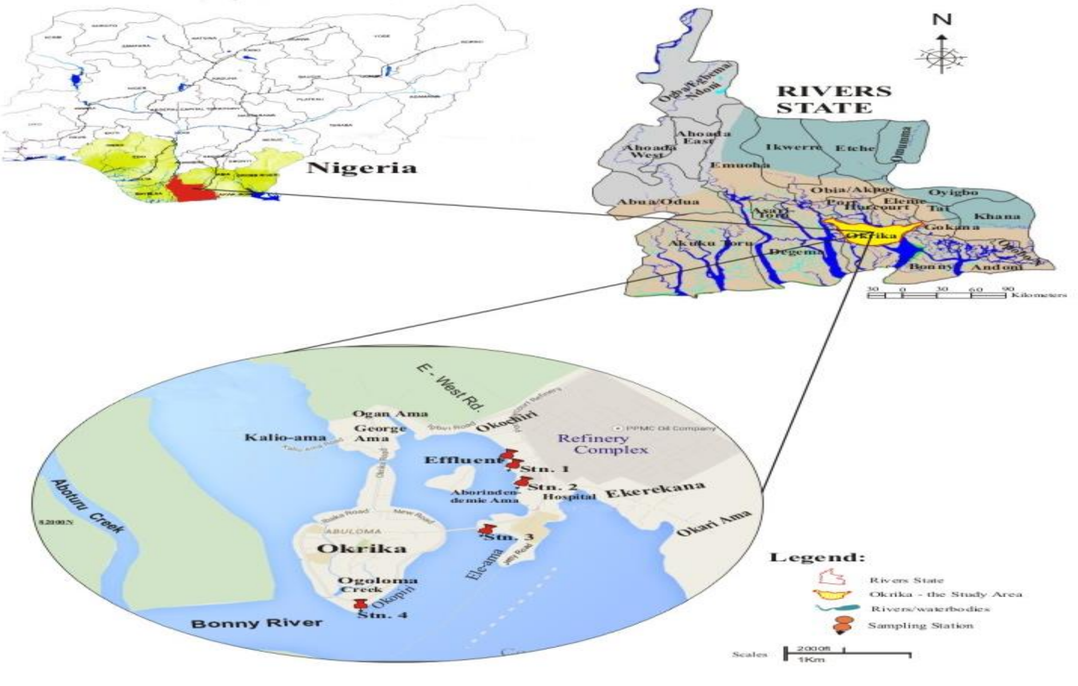

Fig. 1: Map showing the sampling stations in the study area.

Fish Samples: Cast nets were used to collect the fish samples from the four different stations and then immediately labelled and stored in a cool box and then transferred into a freezer in the laboratory prior to analysis.

Fish Samples: The samples were thawed after being brought out of the refrigerator on a clean plastic sheet and a dissecting kit was used to remove the muscles. The tissue was oven-dried and digested with nitric acid and then analysed for manganese, nickel, cobalt and chromium using the Atomic Absorption Spectrophometer (AAS). Concentrations were expressed as mg/kg dry weight.

Statistical Analysis: Statistical analysis was done using descriptive statistics and one-way Analysis of Variance (ANOVA) to test for significant differences between stations or months of sampling.

Results

Manganese concentration in fish muscles (months)

The mean concentration of manganese in September, October, December and January were recorded as 2.73 mg/kg, 1.18 mg/kg, 5.06 mg/kg and 4.10 mg/kg respectively, with the highest mean concentration of 5.06mg/kg obtained in January and the lowest mean concentration of 1.18mg/kg observed in October. The standard deviations for the four months were 2.01, 0.59, 0.83 and 1.97 respectively for September, October, December and January, while standard errors were 1.00, 0.30, 0.42 and 0.99 respectively for the four months. Minimum and maximum values were 1.30, 0.70, 4.20, 2.80; 5.70, 2.00, 6.20, 7.00 respectively for the various months (Fig. 2a).

The results of the analysis of variance revealed a significant disparity between the means of the different months ($p<0.05$).

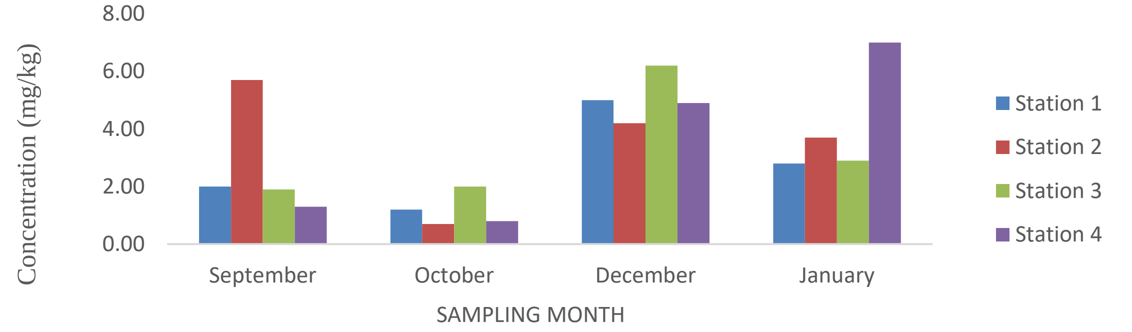

Fig. 2a Manganese concentration in fish muscles (months)

Manganese concentration in fish muscles (stations)

The mean concentration of Manganese in station one, Station 2, Station 3 and Station 4 were recorded as 2.75, 3.58, 3.25 and 3.50mg/kg respectively, with the highest mean concentration of 3.50mg/kg in Station 2 and the lowest mean concentration of 2.75mg/kg in Station 1 as shown in Appendix 6.1.2. The standard deviations for the four stations were calculated to be 1.64, 2.10, 2.02 and 2.96 respectively. Standard error readings were recorded as 0.82, 1.05, 1.01 and 1.48 respectively for the four stations. Minimum and maximum values were 1.20, 0.70, 1.90, 0.80; 5.00, 5.70, 6.20 and 7.00 respectively for the various stations (Fig. 2b). There was no significant difference ($p>0.05$) between the means of the various stations.

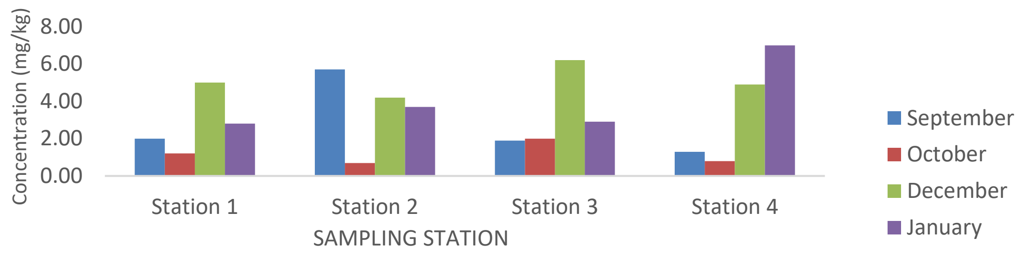

Fig 2b Manganese concentration in fish by stations

Nickel concentration in fish muscles (months)

The mean concentration of Nickel in September, October, December and January were recorded as 2.43, 5.55, 9.10 and 15.15mg/kg respectively, with the highest mean concentration of 15.15mg/kg in January and the lowest mean concentration of 2.43mg/kg in September. Standard deviations for the four months were calculated to be 2.90, 3.32, 4.59 and 4.95 respectively for September, October, December and January. Standard error readings were recorded as 1.45, 1.66, 2.30 and 2.47 respectively for the four months. Minimum and maximum values were 0.20, 3.40, 2.50, 10.60; 6.50, 10.50, 13.00, 20.50 respectively for the various months (Fig. 3a). There was a significant difference among the means of the various months ($p<0.05$).

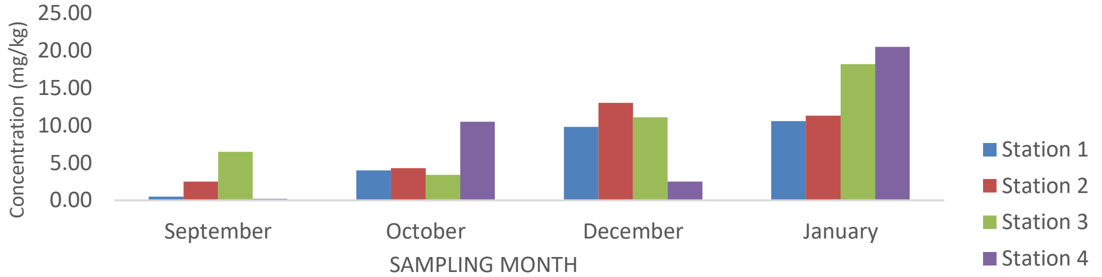

Fig. 3a. Nickel concentration in fish muscles (months)

Nickel concentration in fish muscles (stations)

The mean concentration of Nickel in station one, station two, station three and station four were recorded as 6.22, 7.78, 9.80 and 8.43mg/kg respectively, with the highest mean concentration of 9.80mg/kg in Station 3 and lowest mean concentration of 6.22mg/kg in Station 1. The standard deviation for the four stations was calculated to be 4.82, 5.15, 6.43 and 9.18 respectively. Standard error readings were recorded as 2.41, 2.58, 3.22 and 4.59 respectively for the four stations. Minimum and maximum values were 0.50, 2.50, 3.40, 0.20; 10.60, 13.00, 18.20, 20.50 respectively for the various stations as shown in Fig. 3b. There was no significant difference ($p>0.05$) between the means of the various stations.

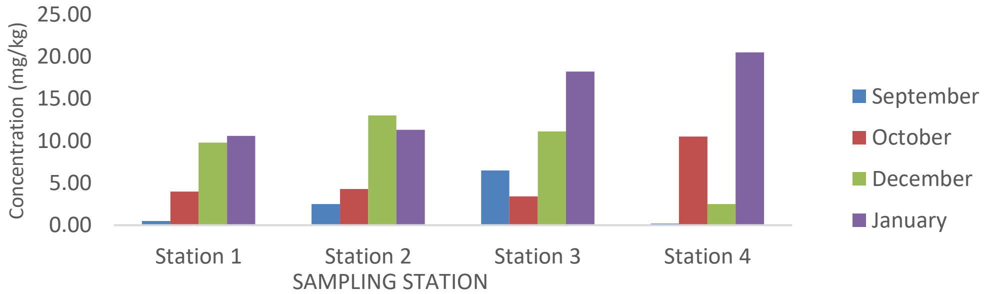

Fig. 3b. Nickel concentration in fish muscles (stations)

Cobalt concentration in fish muscles (months)

The mean concentration of Cobalt in September, October, December and January were 2.00mg/kg, 4.38mg/kg, 8.03mg/kg and 9.03mg/kg respectively, with the highest mean concentration of 9.03mg/kg in January and the lowest mean concentration of 2.00mg/kg in September. The standard deviations for the four months were calculated to be 1.65, 1.49, 2.44 and 2.66 respectively for September, October, December and January. Standard error readings were recorded as 0.83, 0.74, 1.22 and 1.33 respectively for the four months. Minimum and maximum values were 0.20, 2.50, 5.10, 6.20; 3.50, 6.10, 11.00, 12.20 respectively for the various months as presented in Fig. 4a. Analysis of Variance showed a significant difference among the means of the various months ($p<0.05$).

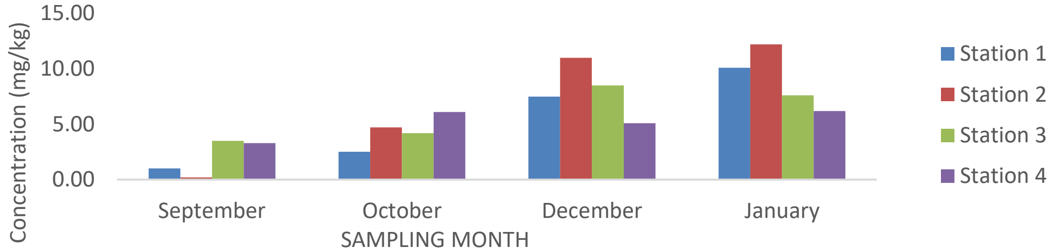

Fig. 4a. Cobalt concentration in fish muscles (months)

Cobalt concentration in fish muscles (stations)

The mean concentration of Cobalt in stations 1 to 4 were recorded as 5.28, 7.03, 5.95 and 5.18mg/kg respectively, with the highest mean concentration of 7.03mg/kg obtained in Station 2 and the lowest mean concentration of 5.18mg/kg in Station 4. The standard deviations for the four stations were calculated to be 4.25, 5.62, 2.47 and 1.35 respectively. Standard error readings were recorded as 2.13, 2.81, 1.24 and 0.67 respectively for the four stations. Minimum and maximum values were 1.00, 0.20, 3.50, 3.30; 10.10, 12.20, 8.50, 6.20 respectively for the various stations (Fig. 4b). There was no significant difference ($p>0.05$) between the means of the various stations.

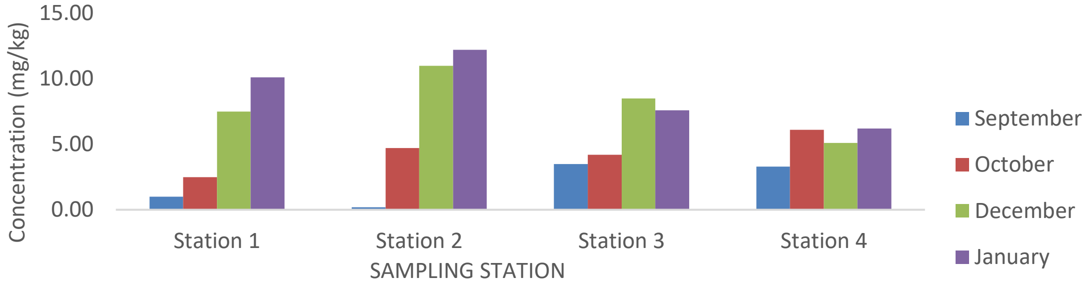

Fig. 4b Cobalt concentration in fish muscles (stations)

Chromium concentration in Muscles of fish

The concentration of chromium in muscles of *Sarotherodon melanotheron* was found to be below the detectable level of 0.05 mg/kg in all samples for the duration of the study.

Discussion of Findings

The study revealed that Nickel analysed in the muscles of the fish was below the safe limits of USFDA for shellfish (USFDA, 1993a, 1993b) and Chromium was below detectable levels. The findings of this research are in contrast with Anaero-Nweke et al. (2018) who reported that "Nickel and Chromium exceeded the permissible limits in the fish muscles from the Upper Bonny Estuary". The findings are also in contrast with the findings of Javed and Usmani (2014) which established that "Ni, Mn and Cr exceeded the limits in the fish muscles and gills. The results of the study showed that the concentrations of heavy metals in the fish muscles were in the following order: Ni>Co>Mn, which is similar to the findings of Owhonda et al. (2016) whose study also showed that Nickel had a high concentration in the fish muscles than the other heavy metals.

Conclusion

The concentrations of manganese, nickel and cobalt in the flesh of *Sarotherodon melanotheron* did not show significant differences between stations and may not but were significantly different between months, so seasonality had more influence than location. The metals that were analysed in the fish muscles were within the safe limits of the United States Department of Food and Drugs Administration (USFDA). There were significant differences between months for all the studied metals. The concentrations of manganese, nickel and cobalt were lower than the DPR target values.

Recommendations

Based on the findings of the study the following recommendations were made:

1. Heavy metal pollution in our aquatic bodies should be closely monitored and the discharge of treated effluents into the Ekerekana creek should be enforced as this will protect humans from heavy metal pollution due to accumulation over time.
2. Also, it is recommended that further studies/continuous monitoring should be done on the levels of various heavy metals especially when the operations of the refinery resume.

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