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Evaluation of Heavy Metal Concentrations in Water, Sediment and Fishes of New Calabar River in Southern Nigeria

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ABSTRACT

The aim of this study was to evaluate the levels of heavy metals in surface water, sediment and selected fish samples in New Calabar River. Samples for analyses were collected for six months across three stations between 08:00 and 12:00 hrs on each sampling day. Physicochemical parameters and metals in water, sediments and tissues of fishes were analyzed following standard procedure using a spectrophotometer. In surface waters, iron, nickel and zinc were above recommended limit while in sediments chromium, iron, nickel, lead and zinc were above the limit. No significant differences were observed in metal concentration in the tissues of the three species. The levels of heavy metals reported in *Chrysichthys nigrodigitatus*, *Tilapia zilli* and *Papyrocranus afer* were higher than that reported in surface waters and sediment, indicating bioaccumulation potentials of metals in fishes. Among the three species, the highest metal concentration was reported in the tissues of *T. zilli* followed by *P. afer* and *C. nigrodigitatus.* The presence of elevated non-essential metals like chromium and lead in fishery products of the New Calabar River requires regular assessment, regulatory and mitigative actions to reduce the burden of metal accumulation in human population through consumption of fishery products.

Keywords: Metal accumulation; New Calabar River; *Chrysichthys nigrodigitatus; Tilapia zilli; Papyrocranus afer*

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Introduction

Environmental pollution, natural or manmade, assumes enormous proportion with the advancement of civilization, industrialization and urbanization. Aquatic ecosystems are one of the most often polluted spheres of the environment. This is because contaminants in air, soil and land ultimately end up in the aquatic ecosystems via precipitation, surface runoff and leaching of rocks and solid wastes (Davies et al. 2009). Municipal sewage, industrial wastewater and agricultural chemicals, mining and petroleum exploration are the main causes of surface water pollution (Yang et al. 2002; Uncumusaoğlu et al. 2016; Akkan et al. 2018). Aquatic ecosystems act as major receptacles for various contaminants generated through the unregulated release of effluents from mines, smelters, industries, and from aerial deposition (Nriagu and Pacyna 1988; Kabata-Pendias 2004; Adriano et al. 2002).

In Nigeria, the input of environmental pollutants in aquatic ecosystems is a common phenomenon. It is a general believe that aquatic systems: inland waters, estuaries, and even the world oceans have an unlimited capacity to absorb increasing amount and variety of wastes and energy from our civilization (Abu and Egenonu 2008). In spite of the global abundance of water and the mainly renewable property of water resources, its carrying capacity has been overwhelmed by anthropogenic discharges of unprecedented quantity of wastes within the last century (Mokaya et al. 2004).

The contamination of freshwaters ecosystems in developing countries with a wide range of pollutants has become a matter of concern for decades (Dahunsi et al. 2012). The growing population and increased industrial activities in many developing countries is also accelerating the exposure of the environment to multiple levels of contaminants including heavy metals. Heavy metals have been considered as major environmental pollutants due to their persistent and toxicity profile in soil, water and biota (Ross 1994; Prasad 2001; Ekperusi et al. 2016) and their biological amplification through the food chain (Dahunsi et al. 2012). Heavy metal contaminants in river system pose serious concern not only to aquatic media, but the human population interacting with such water bodies (Boohene and Agbasah 2018). Metal contamination and the trophic transfer of metals in aquatic food chains has been a subject of concern. More so, locations adjacent to agricultural areas and industrial layouts pose a high risk to aquatic habitats because of the potential for significant runoff and industrial discharges (Ajao et al. 1996; Nubi et al. 2008).

Pollution studies have revealed elevated levels of metals in various river systems in southern Nigeria (Kakulu and Osibanjo 1988; Kakulu and Osibanjo 1992). Consequently, the concentration of metals in Nigerian coastal waters and sediment are of great concern, warranting the need for periodic assessment of both water and aquatic resources in order to monitor the pollution and productivity status of aquatic ecosystem (Ajao et al. 1996; Nubi et al. 2008).

The New Calabar River is among the important water resources in the Niger Delta region and is in the vicinity of the rapidly expanding Port Harcourt metropolis in Rivers State. Local communities within the area are directly dependent on the river for food, agriculture, recreation, and sometimes, domestic water supplies. The fishery resources in the river are exploited in a subsistent manner by the use of different types of traditional fishing gears by local fishermen (Francis and Elenwo 2012). Many fish species belonging to the families Lutjanidae, Clupeidae, Cichlidae and the Claroteidae comprise catches from the river, but the most abundant are the Claroteidae (silver catfish) and Cichlidae (tilapias) (Francis and Elenwo 2012). The river is subject to effluent discharge from industries sited along its banks. Also, surface run-off resulting from soil erosion, lumbering, forestry operations, dredging, and domestic sewage all contributes to a wide scale contamination of the river.

Fin and shell fishes have been widely used as bio-indicators to monitor heavy metals concentration in aquatic environment due to their wide range of distribution and their important position in the food chain (Boohene and Agbasah 2018). Fish can accumulate large amount of toxicants and are considered as one of the most susceptible aquatic organisms to toxic substances present in water (Dahunsi et al. 2012). Fishery products constitute an important aspect of human food due to the high level of protein and essential amino acids for the proper growth and development of the body (Dahunsi et al. 2012; Hadjiliadis 2012). Production of wholesome aquatic foods demands adequate management of the aquatic environment through effective screening for toxicants for corrective actions (Dahunsi et al. 2012). This study aimed to assess the contaminant levels in surface water, sediment, and tissues of selected fish species of New Calabar River to provide a baseline and relevant data for the effective regulation of water and fisheries resources in Nigeria.

Materials and Methods

Study Area

The New Calabar River is located in Port Harcourt, Rivers State. The state is one of the coastal states of the Niger Delta region and the river empties into the Atlantic Ocean (Francis and Elenwo 2012). The Niger Delta region cover a land mass of about some 70,000 km^2 and accounts for about 8% of Nigerian land mass (Onosode and Chokor 2003). The region is characterized by two distinct climatic seasons of wet and dry period. The dry season starts from November to February while the wet season covers March to October with occasional rainfall experienced during the dry season months of November to March. The annual rainfall of the region is between 2,000 and 3,000 mm (Abowei 2000).

The river contains fresh water at its upper and middle reaches but becomes brackish towards the mouth (Figure 1). Anthropogenic activities along the river include an abattoir, poultry, a fabrication company and a weekly market along the bank (Nwadiaro and Ayodele 1992). The University of Port Harcourt is located within the middle reaches of the river. The inhabitants of Choba town make use of New Calabar River for various domestic needs, such as fishing, bathing, cooking and swimming. Also, the river receives the effluent wastewater discharged from Indo-Food Nigeria Plc, defunct Wilbros Nigeria Limited, oil servicing company and an abattoir. Dredging and fishing activities are still prevalent alongside the other numerous human activities.

Sample Stations and Sampling Procedure

Based on the peculiarities observed around the study area, three sampling points were selected within the New Calabar River to reflect different activities in the catchment. The three sampled stations (upstream, midstream and downstream) were approximately 500 meters apart as recommended by national regulation for surface water sampling. All sites were geo-referenced using a handheld global positioning system (GPS) receiver unit (Magellan GPS 315). Station I which is the upstream with latitude 04˚42ʺ02.5ˈN and longitude 07.1˚12ʺ31.3ˈE is close to an abattoir and a waste dump site, station 2 (midstream, latitude 04˚51ʺ58.7ˈN and longitude 006˚53ʺ21.6ˈE) is close to an oil servicing company, while station 3 which is the downstream (latitude 04˚52ʺ58.7ˈN and longitude 006˚53ʺ48.3ˈE) is characterised by human waste disposal and fishing activities. Samples collected for analysis include water, sediment and biota. At each sampling point, three randomize samples were collected to form a composite sample.

The fieldwork was undertaken on a monthly basis from January to June 2019. Surface water sample were collected with a water sampler. Sediment was collected using a sediment sampler. All collected samples were emptied into appropriate sampling bottles, preserved with 10% formalin, labelled properly and kept in ice packs before taken to the laboratory for analysis. Fish samples were purchased from fisherman within the bank of the river after interaction and conforming the location of the catch with respect to the three sampling stations.

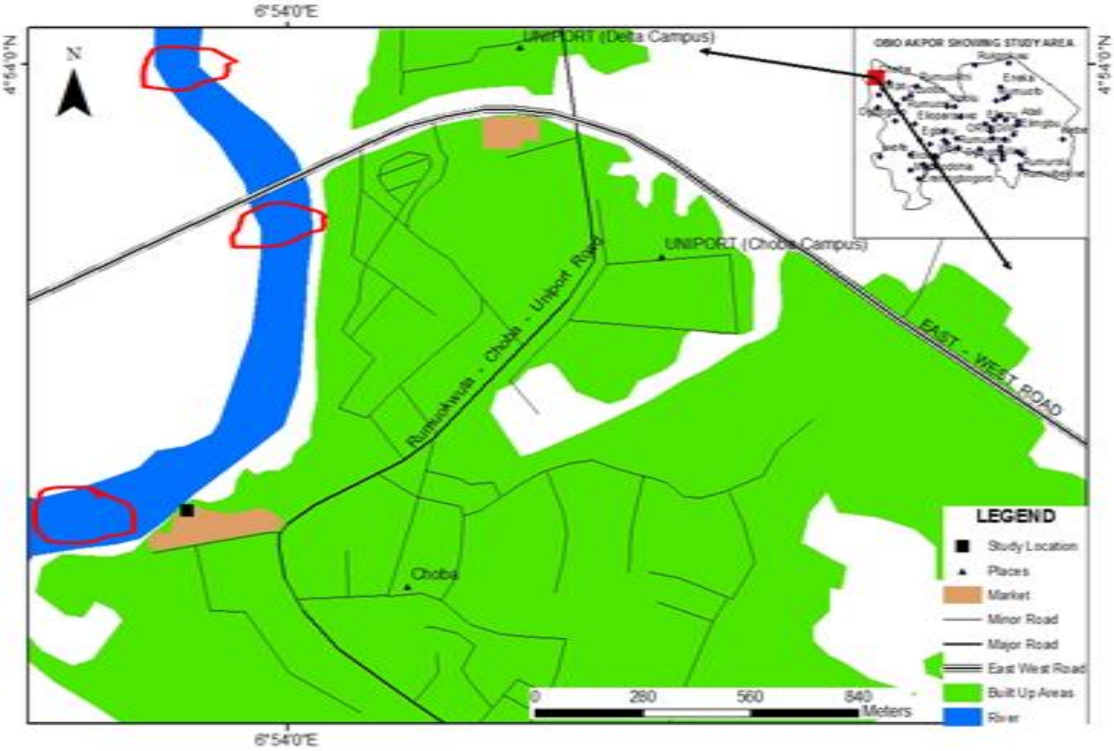

Figure 1. Map of study area showing sampling stations

Determination of Physicochemical Parameters and Heavy Metals

The physicochemical parameters such as temperature, pH, salinity, total dissolved solids (TDS), total suspended solids (TSS), chemical oxygen demand (COD), dissolved oxygen (DO), biochemical oxygen demand (BOD) of the water was measured in the laboratory using Bench-top meter (860033 model) while dissolved oxygen (DO) was measured using Winkler's method. Nitrate, phosphate, sulphate, chloride, ammonia, oil and grease and heavy metal in water and sediments such as Pb, Cr, Cu, Fe, Cd, Zn and Mn were analyzed and recorded following standard laboratory procedure using Atomic Absorption Spectrophotometer (AAS Model API-RP 45). Heavy metals in tissues of selected fish species (*Chrysichthys nigrodigitatus, Tilapia zilli* and *Papyrocranus afer*) were homogenised, extracted with acids, and analyzed using AAS. Also, the bioaccumulation factor (BAF) was determined as the concentration of metals in fishes (mg/kg) over the concentration of metals in sediments (mg/kg).

Data Analysis

The data were analyzed using Statistical Package for Social Sciences (SPSS version 23). Data were summarized into means and standard deviation and were subjected further one-way analysis of variance (ANOVA) to determine significant differences ($P<0.05$). Duncan Multiple Range Test was used to separate significantly different means.

Results

Physicochemical Parameters

The variation in the physicochemical characteristics in surface water of New Calabar River for the sampled period across the three stations is shown in Table 1. All the values except chemical oxygen demand and biochemical oxygen demand were below the WHO recommended limit for freshwater bodies. Across the station, pH, chemical oxygen demand, dissolved oxygen, phosphate, calcium and magnesium were highest in station 1 and lowest in station 3, while phosphate and magnesium were lowest in station 2. Nitrate and sulphate were highest in station 2 and lowest in station 3. Temperature, salinity, total dissolved solids, total suspended solids, biochemical oxygen demand and chloride were highest in station 3 and lowest in station 1, but temperature and biochemical oxygen demand are lowest in station 2. Oil and grease remain the same across the three stations while ammonia was below detection limit in station 2 and 3. Analysis of variance showed there was a significant variation ($P<0.05$; 222.23) among the parameters across the three stations except in pH, temperature, phosphate, ammonia and oil and grease values.

Heavy Metals in Surface Water and Sediments

The variation in the concentration of heavy metals in surface water and sediment of the New Calabar River are shown in Table 2. For heavy metals in surface water, chromium, copper, lead and zinc were highest in station 2. Zinc was lowest in station 1 while the other three metals (chromium, copper and lead) have similar values in station 1 and 3. Iron and manganese were highest in station 3 and lowest in station 1, while nickel was highest in station 1 and lowest in station 3. Cadmium was below detection limit across the sampled stations. No significant differences ($P>0.05$; 0.278) were observed in all the metals in surface waters, except in zinc. All the values of the heavy metals except iron, nickel and zinc were below WHO recommended limit.

For sediments, nickel, lead and zinc were highest in station 2 and lowest in station 1 while copper and manganese were highest in station 1 and lowest in station 3. Chromium was highest in station 3 and lowest in station 1 while iron was highest in station 2 and lowest in station 1. No significant differences ($P>0.05$; 0.114) were observed in all the metals in sediments, except in zinc. All the values of the heavy metals (chromium, iron, nickel, lead, and zinc) except copper and manganese were above WHO recommended limit. Cadmium was below detection limit across the sampled stations.

Table 1. Mean values of physicochemical parameters in surface water at the three stations.

Parameters	Station I (Upstream)	Station II (Midstream)	Station III (Downstream)	WHO 2011
pH	7.42±0.64	7.14±0.41	7.02±0.32	6.5-8.5
Temperature (°C)	28±0.52	27±0.71	28±0.75	30
Salinity (mg/l)	50.4±0.21	60.6±0.10	101±0.11	120
Total Dissolved Solids (mg/l)	140±0.17	180±0.12	220±0.15	250
Total Suspended Solids (mg/l)	120±0.27	160±0.25	240±0.72	1500
Chemical Oxygen Demand (mg/l)	76±0.01	72±0.08	52±0.10	40
Dissolved Oxygen (mg/l)	4.8±0.03	4.4±0.02	4.0±0.01	6
Biological Oxygen Demand (mg/l)	24.8±0.19	23.2±0.21	25.6±0.10	10
Nitrate (mg/l)	2.6±0.02	3.5±0.05	1.8±0.08	50
Phosphate (mg/l)	0.4±0.24	0.33±0.64	0.37±0.46	0.70
Sulphate (mg/l)	6.9±0.28	8.3±0.15	6.9±0.16	250
Chloride (mg/l)	28±1.14	33±1.24	56±1.43	250
Ammonia (mg/l)	0.6±0.03	N.D	N.D	-
Calcium (mg/l)	0.47±0.1	0.35±0.09	0.32±0.07	250
Magnesium (mg/l)	3.14±0.29	2.3±0.31	2.26±0.19	150
Oil and Grease (mg/l)	1±0.001	1±0.001	1±0.001	10

*ND – Not detected

Table 2. Mean concentration of heavy metals in water and sediment of New Calabar River

		Heavy metals (mg/l)							
Stations	**Samples**	**Pb**	**Cr**	**Cu**	**Fe**	**Ni**	**Cd**	**Zn**	**Mn**
I	Sediments	0.14± 0.12	0.17± 0.00	0.10± 0.20	6.8± 0.15	0.19± 0.12	< 0.001± 0.00	2.63± 0.08	0.34± 0.01
	Water	<0.001± 0.02	0.03± 0.10	0.03± 0.07	1.88± 0.05	0.28± 0.05	< 0.001± 0.00	2.43± 0.02	< 0.001± 0.01
II	Sediments	0.32± 0.02	0.18± 0.05	0.18± 0.12	7.06± 0.09	0.62± 0.01	< 0.001± 0.00	6.12± 0.05	0.33± 0.06
	Water	0.06± 0.07	0.04± 0.10	0.05± 0.05	3.06± 0.02	0.25± 0.01	< 0.001± 0.00	6.28± 0.08	0.02± 0.01
III	Sediments	0.25± 0.20	0.22± 0.01	0.13± 0.07	7.03± 0.00	0.28± 0.02	< 0.001± 0.00	2.7± 0.07	< 0.001± 0.12
	Water	<0.001± 0.00	0.03± 0.02	0.03± 0.10	3.07± 0.08	0.19± 0.01	< 0.001± 0.00	3.86± 0.02	0.04± 0.01
Standard Limit	WHO (2011)	0.01	0.05	2.0	0.3	0.02	0.003	0.1	0.4

Heavy Metals in Fishes

The variation observed in heavy metal concentrations in the tissues of *C. nigrodigitatus* are shown in Figure 2. Chromium, copper, iron, manganese, nickel and zinc in the tissues of *C. nigrodigitatus* were highest in station 2 and lowest in station 3, except for copper and iron that were lowest in station 1. Lead was highest in station 3 and lowest in station 1. Cadmium was below detection limit. No significant differences (P>0.05; 0.010) were observed in the means of metals in tissues of *C. nigrodigitatus*. All the values of heavy metals (chromium, iron, nickel, lead and zinc) reported, except copper and manganese were above the WHO acceptable limit for heavy metals in fishery products.

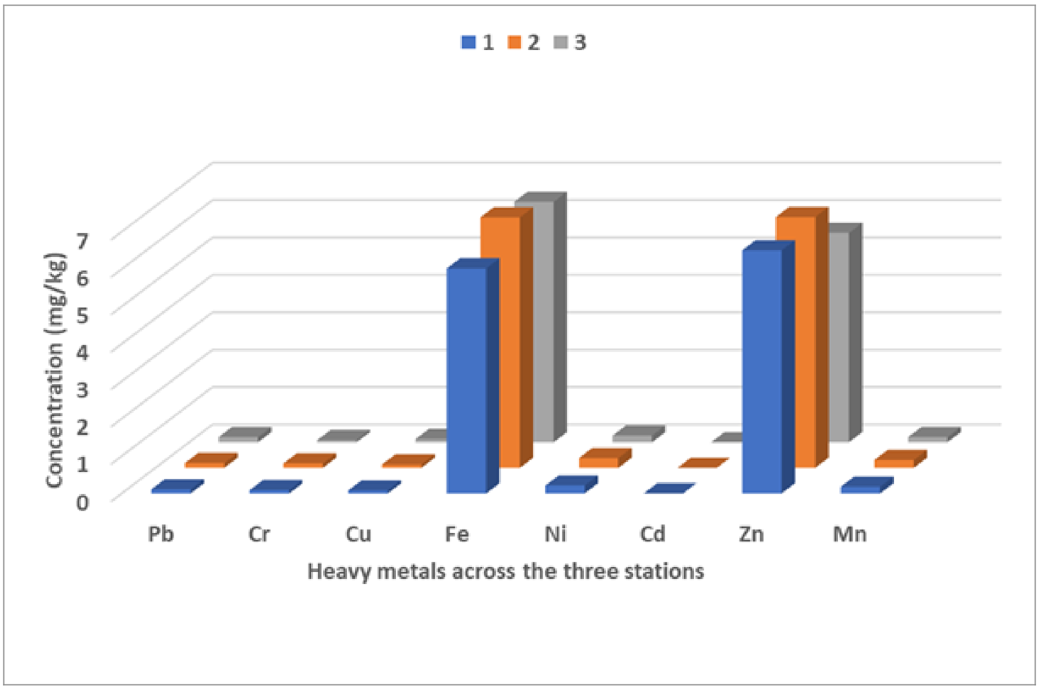

Figure 2. Concentration of heavy metals in tissues of *C. nigrodigitatus*

The concentration of heavy metals observed in the tissues of *T. zilli* is shown in Figure 3. Chromium, copper, nickel, lead and zinc in tissues of *T. zilli* were highest in station 2 and lowest in station 1, except for nickel and zinc that were lowest in station 3. Iron was highest in station 1 and lowest in station 3, while manganese was highest in station 3 and lowest in station 1. Cadmium was below detection limit. No significant differences (P>0.05; 0.002) were observed in the means of metals in tissues of *T. zilli*. All the values of the heavy metals (chromium, iron, nickel, lead and zinc) reported, except copper and manganese were above the acceptable limits for heavy metals concentration in fishes.

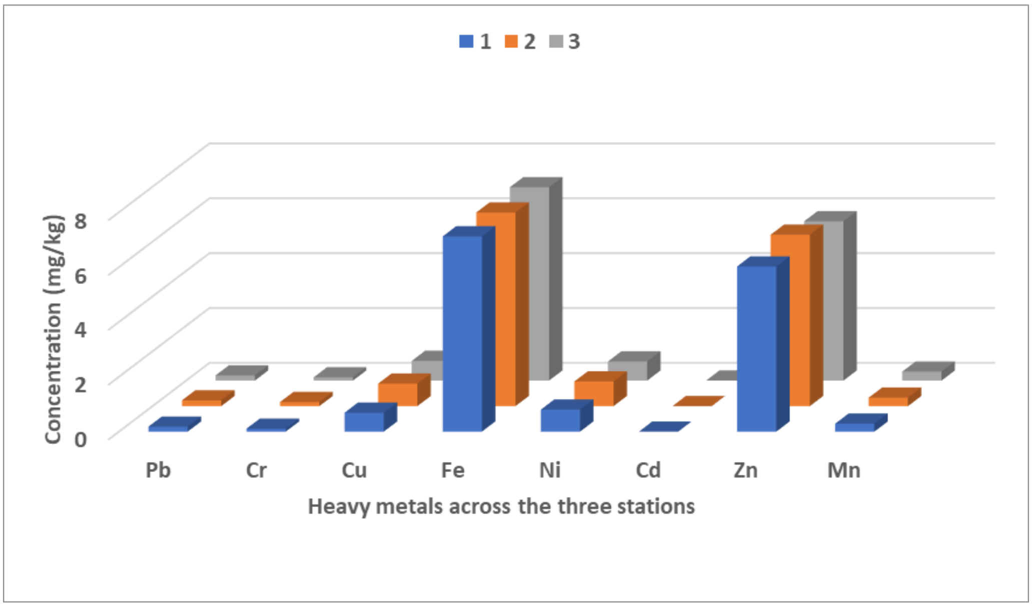

Figure 3. Concentration of heavy metals in tissues of *T. zilli*

The levels of heavy metals recorded in the tissues of *P. afer* are shown in Figure 4. Copper, iron and manganese in tissues of *P. afer* were highest in station 3 and lowest in station 2. Chromium, nickel and lead were highest in station 2 and lowest in station 3, while zinc was highest in station 1 and lowest in station 2. Cadmium was below detection limit. No significant differences (P>0.05; 0.084) were observed in the mean concentration of metals found in tissues of *P. afer*. All the values of the heavy metals (chromium, iron, nickel, lead and zinc) reported, except copper and manganese were above the acceptable limits for heavy metals concentration in fish products.

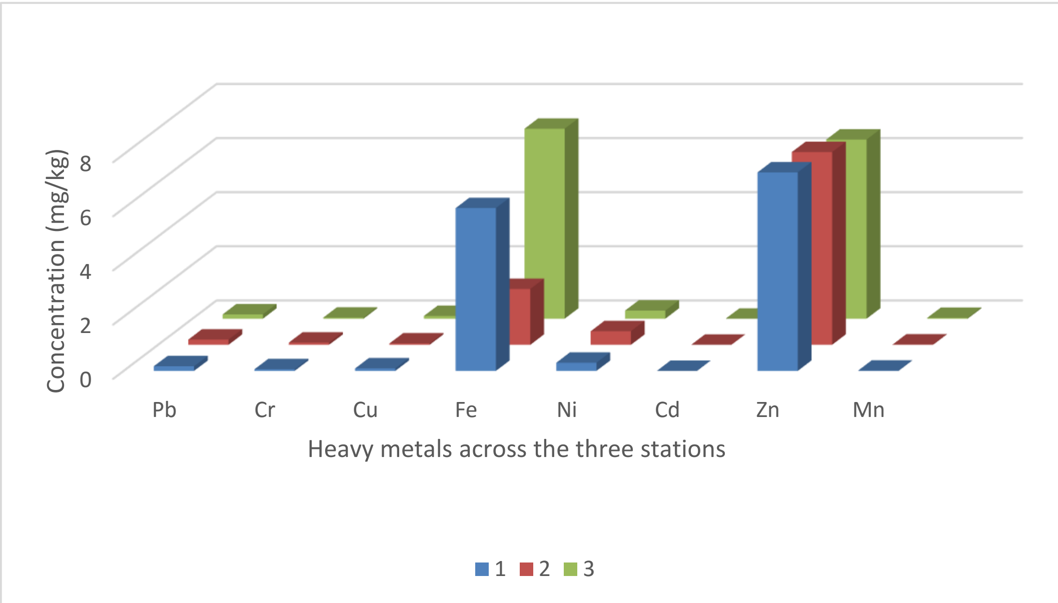

Figure 4. Concentration of heavy metals in tissues of *P. afer*

Bioaccumulation Factor of Metals in Fishes

The bioaccumulation factor (BAF) observed for the three fish species are shown in Table 3.BAF value of *C. nigrodigitatus* was 1.57±0.02, while those of *T. zilli* and *P. afer* were 1.81±0.01 and 1.66±0.03, respectively.

Table 3. Bioaccumulation factor of metals in fish samples at the study area

Fish Samples	BAF
C. nigrodigitatus	1.57±0.02
T. zilli	1.81±0.01
P. afer	1.66±0.03

Discussion

Physicochemical parameters are essential in the assessment of the general water quality condition of a river as it relates to pollution, aquatic biodiversity and river basin management. All the values except chemical and biochemical oxygen demand in surface water of New Calabar River were below the recommended limit for freshwater bodies. Temperature, pH and dissolved oxygen are three intricate parameters that interact in an aquatic ecosystem for the proper functioning of ecological balance. The increase in temperature could directly affects the pH and dissolved oxygen level available to aquatic life. Temperature, pH and dissolved oxygen concentration observed in the upstream of the river is expected, but the elevated levels of chemical oxygen demand beyond recommended limit and sulphate is unusual at the upstream. The factor responsible for the increased sulphate and chemical oxygen demand at upstream maybe unclear but in slow running rivers without obvious elevation in the upstream, mixing of organic nutrients could occur due to turbulence and other anthropogenic activities such as fishing and transportation. Also, the proximity of station 1 to an abattoir and a waste dump site may have resulted in the increased in chemical oxygen demand particularly as a result of precipitation and run-off. The temperature (27.0 - 28.0 ºC) reported in our study, which is within the acceptable limit for freshwater bodies, was similar to those reported in different water bodies in southern Nigeria. The pH values reported in this study, although within permissible limits, tends towards alkalinity of the surface water body. This is expected where rivers have some interaction with saltwater bodies particularly from the mangrove swamp ecosystem in the Niger Delta region. Although dissolved oxygen was the highest in station 1, which is acceptable, it was relatively low (4.0 - 4.8) across the sampled stations. This is a further indication that anthropogenic activities could be affecting the New Calabar River from its pristine condition. The values reported for the three parameters are in conformity with that reported by Adakole et al. (2008), Fianko et al. (2013), Iloba and Ruejoma (2014) and Asibor (2016), but contrasted with that reported by other researchers across Nigeria. Edokpayi and Osimen (2001) and Arimoro (2009) reported lower values for pH and temperature at Ibiekum River, Ekpoma and Adofi River. Jaji et al. (2007) and Asibor (2016) reported lower temperature and pH in Ogun River and Asejire Reservoir, while Arimoro and Ikomi (2008) and Iloba and Ruejoma (2014) reported lower dissolved oxygen levels. Jaji et al. (2007), Ayeni et al. (2011) and Fianko et al. (2013) reported higher temperature, pH and dissolved oxygen compared to our study.

Total dissolved and suspended solids, biochemical and chemical oxygen demand, nitrate, sulphate, phosphate, chloride and ammonia are all pollution indicators in surface water system. The increased levels of these parameters could indicate a growing level of degrading water quality and pollution in the presence of a water body. In this study, all the above parameters were within the acceptable limits for freshwater ecosystems, except biochemical and chemical oxygen demand. The elevation of the two parameters above the permissible limits indicates the changing chemistry of the water body with increased organic nutrients load. The increased level particularly in stations 1 for chemical oxygen demand seems unusual, but this is not new. Sikoki and Anyanwu (2013) reported elevated physicochemical parameters such as total alkalinity, total hardness, conductivity, nitrate-nitrogen, turbidity, biochemical oxygen demand, temperature and phosphate-phosphorus with the highest values at the upstream while pH and dissolved oxygen were highest at midstream of Onu-Iyi-Ukwu Stream. Oluyemi et al. (2010) reported similar nitrate, phosphate and sulphate compared to our study on the physicochemical properties of Ife River, Osun State, Nigeria. Ayeni et al. (2011) and Sikoki and Anyanwu (2013) reported similar values with physicochemical parameters at Ala River, Ondo State and Onu-Iyi-Ukwu Stream in Rivers State. Edokpayi and Osimen (2001), Arimoro et al. (2007), Arimoro and Ikomi (2008), Omoigberale and Ogbeibu (2010), Olomukoro et al. (2013) and Iloba and Ruejoma (2014) reported lower biochemical oxygen demand, chemical oxygen demand, nitrate, phosphate compared to our study in various streams, wetlands and rivers including Agbede Wetlands, Orogodo and Ibiekuma rivers in southern Nigeria. The increased levels of temperature, salinity, total dissolved solids, total suspended solids, biochemical oxygen demand and chloride observed in station 3 was expected at the downstream of the river. Many of the effluents entering the river settles at the downstream. Other anthropogenic factors that may influences the increase in physicochemical parameters at station 3, which include human waste disposal and fishing activities leading to perturbations and disturbances from human interaction at the downstream. Previous authors reported lower physicochemical parameters in rivers in eastern and western Nigeria (Akinbile and Omoniyi 2018; Ayandirana et al. 2018; Anyanwu and Ukaegbu 2019). Ololade and Ajayi (2009) reported higher values for total dissolved solids, chloride, nitrate, sulphate, phosphate but lower biochemical oxygen demand and chemical oxygen demand in major rivers along federal highways in Ondo State. The very low level of oil and grease reported across the three stations in this study indicated that hydrocarbon polluting substances, including petrochemicals, maybe negligible in the New Calabar River system, but the increased and elevated levels of chemical oxygen demand and biochemical oxygen demand above the recommended limit could give an indication of a deteriorating surface water condition of the river.

The levels of chemical distribution in surface waters influence the diversity of life present or adapted to the water column, while sediment act as a sink for contaminants in the aquatic ecosystem and could be an avenue for the recontamination of the water column as a result of turbulence or bioturbation. Among the heavy metals in surface water, only iron and manganese were the highest in station 3. Chromium, copper, lead and zinc were the highest in station 2, while nickel was the highest in station 1. Although station 2 and 3 could be seen to have similar attributes, the increase in nickel at the upstream with values above recommended limits calls for concern. For metals in sediment, only chromium was the highest in station 3. As observed with metals in surface waters, most of the metals such as nickel, lead, iron and zinc were the highest in station 2. This further indicates that anthropogenic activities at station 2, such as wastes from an oil servicing firm, could be impacting the river compared to station 1 and 3. Heavy metals in surface waters and sediment in the Niger Delta are largely associated with effluents or spill from the oil and gas industry or from similar anthropogenic factors within the region (Ekperusi et al. 2016). Copper and manganese were the highest in station 1 for sediments, while nickel was the highest in station 1 for surface waters. This also implies that elevated levels of contaminants are already moving towards the upstream of the river from the midstream, which seems to be more contaminated in this study. Cadmium was below detection limits in surface water and sediment. Omole et al. (2018) also reported cadmium to be below detection limit in surface waters of Atuwara River in western Nigeria. Ololade and Ajayi (2009) reported elevated cadmium levels above recommended limits in four major rivers (Oluwa, Owena, Ogbese and Ose) in Ondo State, Nigeria. Iron in sediment was the highest (7.06), while manganese was the lowest in water (0.001). The increased level of iron in surface water and sediment has been observed by different studies in tropical aquatic ecosystem within the past decade (Fianko et al. 2013; Asare et al. 2018; Asibor 2016). Asibor (2016) and Asareet al. (2018) reported that iron was more abundant than other metals in reservoirs in Nigeria and Ghana. Metals concentration in sediments were higher for all metals compared to the concentration observed in surface waters. This indicated the accumulative and elevated metals deposition in sediments as a sink for contaminants in aquatic ecosystems. It has also been suggested that metals such as cadmium, copper, lead and zinc have a high tendency in binding tenaciously to the organic matter within sediment (Boohene and Agbasah 2018). In the same vein, more metals were above the recommended limits in sediments compared to water column. Other researchers working in various freshwater ecosystems have also reported values similar to our study, but some others reported contrasting observation in the metal profile of freshwater ecosystem across Nigeria. Adebowale et al. (2008) reported similar values for heavy metals in water, but higher values for metals in the sediments of Ondo Estuary, while Ayeni et al. (2011) reported similar values in the surface waters of Ala River, Ondo State. Higher values were reported in surface water of Ife River (Oluyemi et al. 2010), Sakumo and Kpeshi Lagoons, Afam River, Ghana (Laar et al. 2011; Fianko et al. 2013; Boohene and Agbasah 2018), Asejire Reservoir and Atuwara River in western Nigeria (Asibor 2016; Omole et al. 2018). Others reported lower metal levels in Ogun and Ogbese rivers in western Nigeria (Jaji et al. 2007; Akinbile and Omoniyi 2018). Ayandirana et al. (2018) reported lower heavy metals in water, but higher metals (chromium, cadmium, copper, lead, nickel, manganese and zinc) in sediments compared to our study. Nwankwoala and Angaya (2017) also reported elevated levels of copper, chromium and manganese in water and sediments of New Calabar River. Similar values were also reported by George and Abowei (2018) in bottom sediments of the same river.

In surface waters, iron, nickel and zinc were above recommended limit while in sediments chromium, iron, nickel, lead and zinc were above recommended limit. Olu et al. (2019) reported that heavy metals (iron, aluminum, lead, vanadium and cadmium) in surface water and sediments were above permissible limits in Rivers State. The three metals with elevated values in surface waters are basically essential metals, which are required in certain proportions by aquatic organism for proper biological function, but metals such as chromium and lead, which are two of the metals found in elevated levels in sediments, are non-essential or toxic metals and are not known to be useful to biological organisms. The elevated levels of both metals call for more attention to the rising levels of contaminant in the New Calabar River.

Aquatic biodiversity has the potentials to take up and accumulate contaminants in freshwater ecosystem. Many biological agents could magnify contaminants in their tissues beyond the levels present in the environment. The three species reported in this study are staple fishery products consumed by residents and sold in markets across Nigeria, particularly in the Niger Delta region. No significant differences were observed in metal concentration in the tissues of the three species. The levels of heavy metals reported in the tissues of *C. nigrodigitatus*, *T. zilli* and *P. afer* were higher than that reported in surface waters and sediment. This is a clear indication of the potentials of the three species to accumulate heavy metals and transfer it across the food chain. Among the three species, the highest metal concentration was reported in the tissues of *T. zilli*, followed by *P. afer* and *C. nigrodigitatus*. The factor responsible for this is not clear, but *T. zilli* is a fish species that is known to forage widely with increased agility compared to the other two species. An earlier study in the same river by Wegwu and Akaninwor (2006) indicated that the metal concentration (Hg, Pb, Cd, Cu, Cr, Fe, and Zn) in tissues of *Clarias gariepinus* were below the recommended limits. Whereas a recent study by Akankali and Davies (2018) reported above the permissible limits of zinc and lead in the tissues of *Sarotherodon melanotheron*a caught from New Calabar River. This is an indication of the increasing impact of anthropogenic activities along the river bank. Laar et al. (2011) reported elevated levels of iron, copper and manganese and low levels of mercury, chromium and cadmium in Black-chin Tilapia from the Sakumo Lagoon, Ghana. Iron, manganese and zinc concentration in fish were greater than WHO recommended values. The high levels also suggested that the fish were capable of concentrating the metals in their bodies from the aquatic environment. Boohene and Agbasah (2018) reported elevated levels of heavy metals (Co, Cr, Cd, Cu, Mn, Pb, Zn, Fe and Ni) in surface waters, sediments and tissues of *Oreochromis niloticus* in Afram River, Ghana. The values reported were higher than that of reported from our study. Fianko et al. (2013) reported elevated levels of heavy metals (Na, k, Ca, K, Fe, Mn, Ni, Cr, Cd, Al, Pb) in fishes of Kpeshi lagoon compared to our study. In contrast, Ayotunde et al. (2012) observed that copper, cadmium, iron and lead in *C. nigrogitatus* were below the recommended limits in Cross River, Nigeria. They attributed their results to high waste assimilation capacity of the river with respect to chemical dilution, sedimentation and water exchange (Ayotunde et al. 2012). Across the stations, chromium, copper, nickel, lead and zinc in tissues of *T. zilli* were the highest in station 2. Iron was the highest in station 1, while manganese was the highest in station 3. The highest number of metals (chromium, copper, iron, manganese, nickel and zinc) was reported in the tissues of *C. nigrodigitatus* in station 2. Only lead was the highest in station 3. Copper, iron and manganese in tissues of *P. afer* were the highest in station 3. Chromium, nickel and lead were the highest in station 2, while zinc was the highest in station. Cadmium was below the detection limits in the three species. The majority of metals found in the tissues of fish species are mainly from station 2, while few were reported in station 3 and iron alone was the highest in station 1 for *T. zilli*. This also confirmed the pattern of metal distribution in surface waters and sediments. Anthropogenic activities particularly from the oil servicing firm located along the bank of the river at station 2 could be having impact on the water quality of the river. The heavy metals reported in this study are typical of impurities associated with the petrochemical industry via spills and run-offs into soil, surface and groundwater in the Niger Delta region. Fish constitutes the major source of protein for many households, communities and people across the Niger Delta region, due to the relative abundance, quality protein and essential amino acids for the proper growth and functioning of body muscles and tissues (Ayeni et al. 2011). The presence of elevated metals, particularly non-essential metals such as chromium and lead, in the fishery products from the New Calabar River requires regular assessment, regulatory and mitigative actions in order to reduce the burden of metal accumulation in human population due to consumption of fishery products.

In environmental assessment, bioaccumulation factor is one ecological tool for estimating contaminant level in living organisms. In this study, BAF values was calculated as the concentration of heavy metals in sediment over their concentration in fishes. *T. zilli* had the highest bioaccumulation factor followed by *P. afer* and *C. nigrodigitatus*. Ololade and Ajayi (2009) reported higher bioaccumution factors for lead and copper in tissues of *C. gariepinus* collected from four rivers in Ondo State, Nigeria. A BAF value greater than 1 is an indication of efficient uptake of contaminant. In this study, BAF values were higher than 1 for all three species, which indicated high uptake of heavy metals in New Calabar River. The increased uptake of metals reported in the tissues of fishes and the high BAF values are a warning signal for the anthropogenic activities along major rivers in the Niger Delta region and could be introducing contaminants including metals into the food chain.

The assessment of surface water, sediment and fishery products in New Calabar River has given new insights into the changing chemical composition and contaminants fluxes in the aquatic ecosystem. Many of the organic nutrients load were within the acceptable limit for freshwater ecosystem, but the increased and elevated levels of chemical and biochemical oxygen demands, above the recommended limits, could give an indication of a deteriorating surface water condition in the river. The heavy metals concentration in sediments were higher for all metals compared to the concentration observed in surface waters. This indicated the accumulative and elevated metals deposition into sediments as a sink for contaminants in aquatic ecosystems. The levels of heavy metals reported in the tissues of fishes were higher than that reported in surface waters and sediment. This is an indication of the potentials of the three species to accumulate and biomagnify heavy metals across the food chain. The increased uptake of metals reported in the tissues of fishes is a warning signal that anthropogenic activities along the river could be introducing contaminants including metals into the food chain. This requires further attention for the protection of the natural environment, aquatic biodiversity and public health.

References

Abowei JFN. 2000. Aspects of the fisheries of the lower Nun River [PhD Thesis]. University of Port Harcourt. 180 p.

Abu GO, Egenonu C. 2008. The current pollution status of the new Calabar River in the Niger Delta region of Southern Nigeria: A survey of antibiogram profiles of its bacterial isolates. Afr J Environ Sc Technol. 2(6):134-141.

Adakole JA, Abulode DS, Balarabe ML. 2008. Assessment of Water Quality of a Man-Made Lake in Zaria, Nigeria. Paper presented at: The 12th World Lake Conference; Jaipur, India.

Adebowale KO, Agunbiade FO, Olu-Owolabi BI. 2008. Fuzzy comprehensive assessment of metal contamination of water and sediments in Ondo Estuary, Nigeria. Chem Ecol. 24(4):269-283. doi: 10.1080/02757540802255600

Adriano DC, Weber J, Bolan NS, Paramasivam S, Koo BJ, Sajwan KS. 2002. Effects of high rates of coal fly ash on soil, turfgrass, and groundwater quality. Water Air SoilPoll. 139(1-4):365-385. doi: 10.1023/A:1015895922471

Ajao EA, Okoye BCO, Adekanmbi EO. 1996. Environmental pollution in the Nigerian Coastal Waters. A case study of the Lagos Lagoon. Water Quality Monitoring and Environmental Status in Nigeria. FEPA Monograph. 6:101-112.

Akankali JA, Davies IC. 2018. Assessment of heavy metal pollutants (Zn & Pb) in New Calabar River, Niger delta, Nigeria. International Journal of Fisheries and Aquatic Studies. 6(2):436-441.

Akinbile CO, Omoniyi O. 2018. Quality assessment and classification of Ogbese River using water quality index (WQI) tool. Sustain Wat Resour Managem. 4:1023-1030. doi: 10.1007/s40899-018-0226-8

Akkan T, Yazicioglu O, Yazici R, Yilmaz M. (2018).Assessment of irrigation water quality of Turkey using multivariate statistical techniques and water quality index: Sıddıklı Dam Lake. Desalin WaterTreat.115:261-270. doi: 10.5004/dwt.2018.22302

Anyanwu ED, Ukaegbu AB. 2019. Index approach to water quality assessment of a south eastern Nigerian river. Int J Fish Aquat Stud. 7(1):153-159.

Arimoro FO. 2009. Impact of Rubber Effluent Discharges on the Water Quality and Macroinvertebrate Community Assemblages in a Forest Stream in Niger Delta. Chemosphere. 77(3):440-449. doi: 10.1016/j.chemosphere.2009.06.031

Arimoro FO, Ikomi RB. 2008. Response of macroinvertebrates to abattoir wastes and other anthropogenic activities in a municipal stream in the Niger Delta, Nigeria. The Environmentalist. 28:85-98. doi: 10.1007/s10669-007-9033-8

Arimoro FO, Ikomi RB, Efemuna E. 2007. Macroinvertebrate Community Patterns and Diversity in Relation to Water Quality Status of River Ase, Niger Delta, Nigeria. J Fish Aquat Sci.2(5):337-344. doi: 10.3923/jfas.2007.337.344

Asare ML, Cobbina SJ, Akpabey FJ, Duwiejuah AB, Abuntori ZN. 2018. Heavy Metal Concentration in Water, Sediment and Fish Species in the Bontanga Reservoir, Ghana. Toxicol Environ Health Sci. 10: 49-58. doi: 10.1007/s13530-018-0346-4

Asibor IG. 2016. Assessment of Heavy Metals Associated with bottom Sediment of Asejire Reservoir, Southwest Nigeria. Int Lett Nat Sci. 55:9-16. doi: 10.18052/www.scipress.com/ILNS.55.9

Ayandirana TA, Fawole OO, Dahunsi SO. 2018. Water quality assessment of bitumen polluted Oluwa River, South-Western Nigeria. Wat Resour Ind. 19:13-24. doi: 10.1016/j.wri.2017.12.002

Ayeni IAO, Balogun II, Soneye ASO. 2011. Seasonal Assessment of Physico-chemical concentration of polluted urban river: A Case of Ala River in Southwestern-Nigeria. Res J Environ Sci.5(1):22-35. doi: 10.3923/rjes.2011.22.35

Ayotunde EO, Offem BO, Ada FB. 2012. Heavy metal profile of water, sediment and freshwater cat fish, *Chrysichthys nigrodigitatus* (Siluriformes: Bagridae) of Cross River, Nigeria. Rev Biol Trop. 60(3): 1289-1301.

Boohene M, Agbasah W. 2018. Levels of heavy metals in water, fish (*Oreochromis niloticus*) and sediment from the Afram River, Ghana. Haya: The Saudi J Life Sci. 3(3):259-268. doi: 10.21276/haya.2018.3.3.7

Dahunsi SO, Oranusi SU, Ishola RO. 2012. Differential bioaccumulation of heavy metals in selected biomarkers of *Clarias gariepinus* (Burchell, 1822)

exposed to chemical additives effluent. J Res Environ Sci Toxicol.1(5):100-106.
Davies OA, Abowei JFN, Tawari CC. 2009. Phytoplankton Community of Elechi Creek, Niger Delta, Nigeria-A Nutrient-Polluted Tropical Creek. Amer J Appl Sci. 6(6):1143-1152. doi: 10.3844/ajassp.2009.1143.1152
Edokpayi CA, Osimen CO. 2001. Hydrobiological Studies on Ibiekuma River at Ekpoma, Southern Nigeria, after Impoundment: the Faunal Characteristics. Afr J Sci Tech.2(1):72-81. doi: 10.4314/ajst.v2i1.44647
Ekperusi OA, Aigbodion IF, Iloba BN, Okorefe S. 2016. Assessment and bioremediation of heavy metals from crude oil contaminated soil by earthworms. Ethiopian J Environ Stud Managem. 9(2):1036-1046. doi: 10.4314/ejesm.v9i2.9S
Fianko JR, Laar C, Osei J, Anim AK, Gibrilla A, Adomako D. 2013. Evaluation of some heavy metal loading in the Kpeshi lagoon, Ghana. Appl Water Sci. 3:311-319. doi: 10.1007/s13201-013-0083-4
Francis A, Elenwo U. 2012. Aspects of the biology of trap caught *Chrysichthys nigrodigitatus* (Lacepede: 1803) from the New Calabar River, Nigeria. Int J Fish Aquacult.4(6):99-104. doi: 10.5897/IJFA11.087
George ADI, Abowei JFN. 2018. Physical and Chemical Parameters and Some Heavy Metal for Three Rainy Season Months in Water and Sediments of Upper New Calabar River, Niger Delta, Nigeria. Open Access LibraryJournal.5:1-4. doi: 10.4236/oalib.1104456
Godwin AI. 2016. Assessment of Heavy Metals Associated with bottom Sediment of Asejire Reservoir, Southwest Nigeria. Int Lett Nat Sci. 55:9-16. doi: 10.18052/www.scipress.com/ILNS.55.9
Hadjiliadis N. (Ed.). 2012. Cytotoxic, mutagenic and carcinogenic potential of heavy metals related to human environment (Vol. 26). Przesieka, Poland: Springer Science & Business Media 629 p.
Iloba KI, Ruejoma MGO. 2014. Physico-chemical characteristics and zooplankton of Ekpan River, Delta State, Nigeria. IJABR.6(1):8-30.
Jaji MO, Bamgbose O, Odukoya OO, Arowolo TA. 2007. Water quality assessment of Ogun River, South West Nigeria. Environ Monit Assess. 133:473-482. doi: 10.1007/s10661-006-9602-1
Kabata-Pendias A. 2004. Soil-plant transfer of trace elements-an environmental issue. Geoderma. 122(2-4):143-149. doi: 10.1016/j.geoderma.2004.01.004
Kakulu SE, Osibanjo O. 1988. Trace heavy metal pollutional studies in sediments of the Niger Delta area of Nigeria. J Chem Soc Nigeria. 13:9-15.
Kakulu SE, Osibanjo O. 1992. Pollution studies of Nigerian rivers: trace metal levels in the Niger Delta area of Nigeria. Int J Environ Stud. 41(3-4):287-292. doi: 10.1080/00207239208710768
Laar C, Fianko JR, Akiti TT, Osae S, Brimah AK. 2011. Determination of heavy metals in the Black-Chin Tilapia from the Sakumo Lagoon, Ghana. Res J Environ Earth Sci. 3(1):8-13.
Mokaya SK, Mathooko JM, Leichtfried M. 2004. Influence of anthropogenic activities on water quality of a tropical stream ecosystem. Afr J Ecol. 42(4): 281-288. doi: 10.1111/j.1365-2028.2004.00521.x
Nriagu JO, Pacyna JM. 1988. Quantitative assessment of worldwide contamination of air, water and soils by tracemetals. Nature. 333:134-139. doi: 10.1038/333134a0
Nubi OA, Osibanjo O, Nubi AT. 2008. Impact assessment of dumpsite leachate on the qualities of surface water and sediment of river Eku, Ona-Ara Local Government, Oyo State, Nigeria. Sci World J. 3(3): 22-31. doi: 10.4314/swj.v3i3.51813
Nwadiaro CS, Ayodele ROO. 1992. Contribution to the biology of *Sarotherodon melanotheron* in the New Calabar River (Nigeria). Acta Hydrobiol. 34(3): 287-300.
Nwankwoala HO, Angaya YB. 2017. An evaluation of heavy metals concentration in the Choba section of the New Calabar River, Eastern Niger Delta. Biodiversity IntJ.1(6):62-68. doi: 10.15406/bij.2017.01.00030
Ololade IA, Ajayi AO. 2009. Contamination profile of major rivers along the highways in Ondo State, Nigeria. J Toxicol Environ Health Sci. 1(3):038-053.
Olomukoro JO, Osamuyiamen IM, Dirisu AR. 2013. Ecological Survey of Macrobenthic Invertebrates of Selected Ponds in Agbede Flood Plain, Southern Nigeria. J Biol Agr Healthc. 3(10):23-29.
Olu U, Ugbomeh AP, Bob Manuel KNO, Ekweozor IKE. 2019. Levels of Selected Heavy Metals in Water and Sediment of the Soku Oil Field Area of the Niger Delta, Nigeria. J Aquat Pollut Toxicol. 3(1):25-35
Oluyemi EA, Adekunle AS, Adenuga AA, Makinde WO. 2010. Physico-chemical properties and heavy metal content of water sources in Ife North Local Government Area of Osun State, Nigeria. Afr J Environ Sci Technol. 4(10):691-697.
Omoigberale MO, Ogbeibu AE. 2010. Environmental Impacts of Oil exploration and production on the invertebrate fauna of Osse River, Southern Nigeria. Res J Environ Sci. 4(2):101-114. doi: 10.3923/rjes.2010.101.114
Omole DO, Ogbiye AS, Longe EO, Adewumi IK, Elemile OO, Tenebe TI. 2018. Water quality checks on River Atuwara, south-west Nigeria. Wit Trans Ecol Environ. 228:165-173. doi:10.2495/WP180171
Onosode GO, Chokor BA 2003. Environmental issues and challenges of the Niger Delta: perspectives from the Niger Delta Environmental Survey process: selected speeches and presentations, 1995-2001. Lagos: Lilybank Property & Trust Limited 278 p.
Prasad MNV. 2001. Cadmium toxicity and tolerance in vascular plants. Environ Exp Bot. 35(4):525-545. doi: 10.1016/0098-8472(95)00024-0
Ross SM. 1994. Sources and forms of potentially toxic metals in soilplant systems. In: Ross SM, editor. Toxic

metals in soil- plant systems. New York: Wiley and Sons. p. 3-25.

Sikoki FD, Anyanwu IN. 2013. Spatial and Temporal Variations of Physicochemical Variables in a Small Pristine Stream in Niger Delta, Nigeria. J Fish Aquat Sci.8(1):129-135. doi: 10.3923/jfas.2013.129.135

Uncumusaoglu AA, Sengul U, Akkan T. 2016. Environmental contamination of heavy metals in the yaglidere stream (Giresun), Southeastern Black Sea. Fresenius Environ Bull. 25(12):5492-5498.

Wegwu MO, Akaninwor JO. 2006. Assessment of Heavy- Metal Profile of the New Calabar River and Its Impact on Juvenile *Clarias gariepinus*. Chem Biodivers.3(1):79-87 doi: 10.1002/cbdv.200690010

Yang H, Rose NL, Battarbee RW. 2002. Distribution of some trace metals in Lochnagar, a Scottish mountain lake ecosystem and its catchment. Sci Total Environ. 285(1-3): 197-208. doi: 10.1016/s0048-9697(01)00931-7